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# Distributions of brominated organic compounds in the troposphere and lower stratosphere

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**Abstract.** A comprehensive suite of brominated organic compounds was measured from whole air samples collected during the 1996 NASA Stratospheric Tracers of Atmospheric Transport aircraft campaign and the 1996 NASA Global Tropospheric Experiment Pacific Exploratory Mission-Tropics aircraft campaign. Measurements of individual species and total organic bromine were utilized to describe latitudinal and vertical distributions in the troposphere and lower stratosphere, fractional contributions to total organic bromine by individual species, fractional dissociation of the long-lived species relative to CFC-11, and the Ozone Depletion Potential of the halons and  $\text{CH}_3\text{Br}$ . Spatial differences in the various organic brominated compounds were related to their respective sources and chemical lifetimes. The difference between tropospheric mixing ratios in the Northern and Southern Hemispheres for halons was approximately equivalent to their annual tropospheric growth rates, while the interhemispheric ratio of  $\text{CH}_3\text{Br}$  was 1.18. The shorter-lived brominated organic species showed larger tropospheric mixing ratios in the tropics relative to midlatitudes, which may reflect marine biogenic sources. Significant vertical gradients in the troposphere were observed for the short-lived species with upper troposphere values 40–70% of the lower troposphere values. Much smaller vertical gradients (3–14%) were observed for  $\text{CH}_3\text{Br}$ , and no significant vertical gradients were observed for the halons. Above the tropopause, the decrease in organic bromine compounds was found to have some seasonal and latitudinal differences. The combined losses of the individual compounds resulted in a loss of total organic bromine between the tropopause and 20 km of 38–40% in the tropics and 75–85% in midlatitudes. The fractional dissociation of the halons and  $\text{CH}_3\text{Br}$  relative to CFC-11 showed latitudinal differences, with larger values in the tropics.

## 1. Introduction

The source of reactive bromine in the stratosphere is from a variety of organic bromine-containing trace gases with both natural and anthropogenic origins. The mixing ratios of organic bromine-containing source gases entering the stratosphere have been measured directly from whole air samples [Fabian *et al.*, 1994; Daniel *et al.*, 1996; Schauffler *et al.*, 1998] and inferred from tropospheric measurements [Montzka *et al.*, 1996; Wamsley *et al.*, 1998]. Presently, the primary organic source gases of bromine to the lower stratosphere are methyl bromide ( $\text{CH}_3\text{Br}$ ), halon 1211 ( $\text{CBrClF}_2$ ), halon 1301 ( $\text{CBrF}_3$ ), halon 2402 ( $\text{CBrF}_2\text{CBrF}_2$ ), and dibromomethane ( $\text{CH}_2\text{Br}_2$ ) [Schauffler *et al.*, 1993; Fabian *et al.*, 1994; Kourtidis *et al.*, 1996, 1998; Schauffler *et al.*, 1998]. Additional source gases of organic bromine in the upper troposphere include bromoform ( $\text{CHBr}_3$ ),

bromochloromethane ( $\text{CH}_2\text{BrCl}$ ), bromodichloromethane ( $\text{CHBrCl}_2$ ), and dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ) [Schauffler *et al.*, 1998]. The total amount of organic bromine source gases at the tropical tropopause in 1996 was  $17.4 \pm 0.9$  ppt with most of the variability due to variations in the mixing ratios of short-lived halogenated methanes [Schauffler *et al.*, 1998].

The participation of bromine in stratospheric ozone loss occurs via catalytic cycles that also involve  $\text{Cl}_x$ ,  $\text{NO}_x$ , and  $\text{HO}_x$  species [Solomon *et al.*, 1986; McElroy *et al.*, 1986; Anderson *et al.*, 1989; Solomon, 1990; Salawitch *et al.*, 1993; Garcia and Solomon, 1994; Wennberg *et al.*, 1994]. Bromine is more efficient than an equivalent amount of chlorine in the catalytic destruction of ozone because a larger fraction of the total inorganic bromine is in a reactive form relative to that of inorganic chlorine [Solomon *et al.*, 1992; Garcia and Solomon, 1994]. The magnitude of the efficiency difference between bromine and chlorine has been estimated to be from 40 to 400 [Solomon *et al.*, 1992; Garcia and Solomon, 1994; Daniel *et al.*, 1995]. This efficiency difference, or  $\alpha$ , is variable with altitude and chlorine loading in the stratosphere. Bromine may be placed on an equivalent scale with chlorine by multiplying  $\alpha$  by the total

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amount of inorganic bromine. This value is then added to the inorganic chlorine to give an equivalent chlorine loading [Daniel *et al.*, 1995; Montzka *et al.*, 1996]. Equivalent effective stratospheric chlorine (EESC), calculated with an  $\alpha$  of 40, was used by Daniel *et al.* [1995] to evaluate halogen loading, ozone loss, and the resulting effects on radiative forcing between 1950 and 2100. Montzka *et al.* [1996] used effective equivalent chlorine calculations based on an  $\alpha$  of 100 and tropospheric measurements of chlorine and bromine source gases to determine the effects of recent changes in the growth rates of these gases on chlorine loading in the stratosphere. In studies such as these, accurate measurements of organic source gases in the lower stratosphere provide important constraints on the amount of inorganic bromine available from these sources.

High-resolution measurements of organic source gases of bromine across the tropopause in various latitude regimes are required to describe the vertical structures that result from both local chemistry and transport. Vertical distributions of individual organic bromine compounds may be used: (1) to accurately determine the amount and distribution of organic bromine in both the troposphere and lower stratosphere; (2) to evaluate the variability of organic bromine in these regions; (3) to calculate the amount of inorganic bromine in the lower stratosphere; (4) to evaluate loss processes in both regimes; and (5) to calculate the vertical distribution of individual species contributions to total organic and inorganic bromine. In addition, the measured correlations between organic halogen trace gases are a useful tool in evaluating model chemical schemes [Avallone and Prather, 1997], in calculations of the fractional halogen release of a given compound relative to CFC-11 ( $\text{CCl}_3\text{F}$ ), which is required for determining the ozone depletion potential (ODP) of organic halogens [Solomon *et al.*, 1992], and in calculations of stratospheric lifetimes of trace gases [Avallone and Prather, 1997; Volk *et al.*, 1997]. A number of additional investigations have used two and three-dimensional modeled correlations to describe the theory of trace gas correlations [Plumb and Ko, 1992; Hall and Prather, 1995; Plumb, 1996].

In this paper we present a comprehensive suite of measurements of brominated organic compounds in the upper troposphere and lower stratosphere from the NASA Stratospheric

Tracers of Atmospheric Transport (STRAT) Campaign in January/February, July/August, and December 1996 and in the mid-lower troposphere from the 1996 August/September NASA Global Tropospheric Experiment (GTE) Pacific Exploratory Mission-Tropics (PEM Tropics) Campaign. The comprehensive nature of this paper requires extensive use of figures to adequately represent the measurements discussed. For the individual species and total organic bromine we discuss the upper tropospheric mixing ratios from the three STRAT deployments by latitude regions and then compare the tropospheric mixing ratios from the July/August STRAT deployment with the PEM Tropics values. Then we show vertical profiles in the tropics and midlatitudes from the two campaigns. We also compare the January/February STRAT measurements with the July/August STRAT measurements. In the total organic bromine section, we discuss vertical contributions of the individual species to total organic bromine from the STRAT measurements. Finally, we calculate the fractional dissociation of each major species relative to  $\text{CCl}_3\text{F}$  and use this value to calculate the respective ODPs.

## 2. Background Information on Brominated Organic Compounds in the Atmosphere

The halons currently represent ~38% of the organic bromine at the tropical tropopause [Schauffler *et al.*, 1998]. The halons have anthropogenic sources and are used primarily as fire extinguishers. Halon surface measurements demonstrate increasing mixing ratios over the last decade [Butler *et al.*, 1998]. The  $\text{CBrClF}_2$  growth rate has been relatively constant while that of  $\text{CBrF}_3$  has decreased over the last few years.  $\text{CBrF}_2\text{CBrF}_2$  showed a small increase in mixing ratios in recent years. Table 1 includes the global average halon surface mixing ratios at the end of 1996, the atmospheric lifetimes, and the ODPs. The relatively high ODPs of the halons led to the prohibition of their manufacture in developed countries as of January 1994, with continued production in developing countries until the year 2002, when production will be frozen at 1995-1997 levels [United Nations Environmental Programme (UNEP) 1992]. Recent calculations suggest that the potential level of emissions from halons already produced by developed countries and not yet

**Table 1.** Lifetimes, ODPs, and Tropospheric Mixing Ratios of Organic Bromine Compounds

	$\text{CH}_3\text{Br}$	$\text{CBrF}_3$	$\text{CBrClF}_2$	$\text{C}_2\text{Br}_2\text{F}_4$	
Lifetime, years	0.7 <sup>a</sup>	65 <sup>b</sup>	20 <sup>b</sup>	20 <sup>c</sup>	
ODP	0.43 <sup>a</sup>	13 <sup>d</sup>	5 <sup>d</sup>	6.1 <sup>d</sup>	
Average mixing ratio, ppt	10 <sup>a</sup>	2.3 <sup>e</sup>	3.5 <sup>e</sup>	0.45 <sup>e</sup>	
	$\text{CH}_2\text{Br}_2$	$\text{CHBr}_2\text{Cl}$	$\text{CHBr}_3$	$\text{CH}_2\text{BrCl}$	$\text{CHBrCl}_2$
Lifetime, years	0.3-0.4 <sup>f,j</sup>	0.1 <sup>g</sup>	0.1 <sup>i</sup>	0.4 <sup>g</sup>	0.1 <sup>g</sup>
ODP	0.10-0.15 <sup>f,j</sup>	nd	nd	nd	nd
Average mixing ratio, ppt	<1.5 <sup>h</sup>	<0.5 <sup>h</sup>	<2.0 <sup>h</sup>	<0.5 <sup>h</sup>	<0.5 <sup>h</sup>

ODP, ozone depletion potential; nd, not determined

<sup>a</sup>Butler and Rodriguez [1996].

<sup>b</sup>Ko and Jackman [1994].

<sup>c</sup>Burkholder *et al.* [1991].

<sup>d</sup>Solomon *et al.* [1995].

<sup>e</sup>Butler *et al.* [1998].

<sup>f</sup>Mellouki *et al.* [1992].

<sup>g</sup>Bilde *et al.* [1998].

<sup>h</sup>Class and Ballschmiter [1988], Atlas *et al.* [1993], Schall and Heumann [1993], Atlas and Ridley [1996], and Yokouchi *et al.* [1997].

<sup>i</sup>Moortgat *et al.* [1993].

<sup>j</sup>Zhang *et al.* [1997].

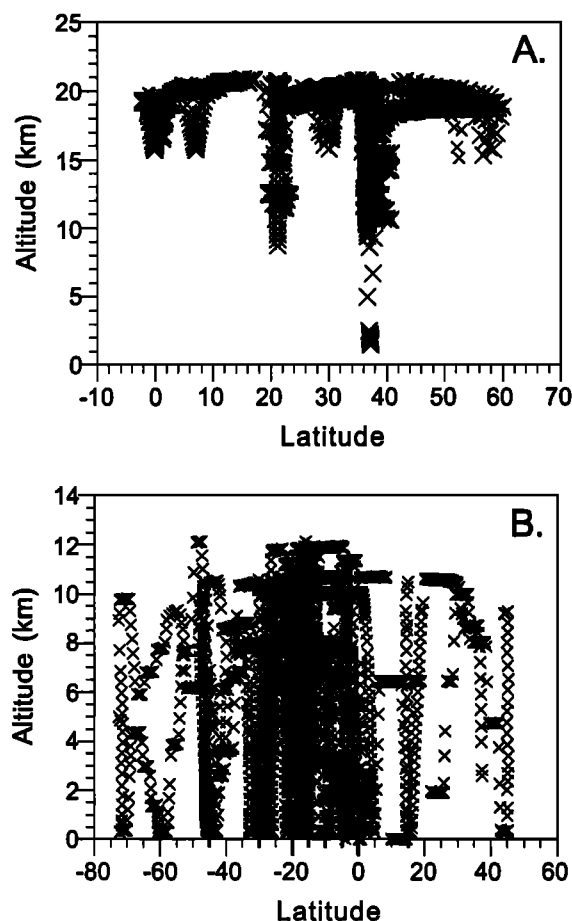
released will continue to be an important source of bromine to the stratosphere over the next few decades [Butler *et al.*, 1998].

Methyl bromide represents ~55% of the organic bromine at the tropical tropopause [Schauffler *et al.*, 1998; Kourtidis *et al.*, 1998]. Methyl bromide has both natural and anthropogenic sources. Recent summaries of published information on  $\text{CH}_3\text{Br}$  are given by Butler and Rodriguez [1996] and Penkett *et al.* [1995]. The primary use of industrially produced  $\text{CH}_3\text{Br}$  is fumigation. Additional sources of  $\text{CH}_3\text{Br}$  are from burning of leaded gasoline and from biomass burning [Penkett *et al.*, 1995; Andreae *et al.*, 1996; N.J. Blake *et al.*, 1996; Thomas *et al.*, 1997]. A primary natural source is believed to be the oceans, which also represent an important sink [Lobert *et al.*, 1995; Yvon-Lewis and Butler, 1997; Lobert *et al.*, 1997]. Additional sinks are reaction with OH, photolysis in the stratosphere and uptake by soils, aquatic bacteria, and plants [Gillotay *et al.*, 1988; Mellouki *et al.*, 1992; Zhang *et al.*, 1992; Shorter *et al.*, 1995; Connell *et al.*, 1997; Jeffers *et al.*, 1998]. A slight increase in surface mixing ratios between 1988 and 1992 from measurements [Khalil *et al.*, 1993] and between 1970 and 1990 from calculations based on agricultural usage [Singh and Kanakidou, 1993] has been reported; however, the variability in measured data and the small database prevent reliable quantitative estimates of a trend [Penkett *et al.*, 1995]. Samples collected from South Pole firm air indicate Southern Hemisphere  $\text{CH}_3\text{Br}$  mixing ratios were ~25% lower near the beginning of this century than in 1996 [Elkins *et al.*, 1996]. The global average mixing ratio, lifetime, and ODP of  $\text{CH}_3\text{Br}$  are shown in Table 1. The production of  $\text{CH}_3\text{Br}$  for use by developed countries has been capped at 1991 levels since 1995 under the terms of the Montreal Protocol and subsequent amendments [UNEP, 1992].

Dibromomethane, bromochloromethane, and bromodichloromethane currently represent ~6–10%, 0.7%, and 0.1%, respectively, of organic bromine at the tropical tropopause [Schauffler *et al.*, 1993; Kourtidis *et al.*, 1996; Schauffler *et al.*, 1998].  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$ , and  $\text{CH}_2\text{BrCl}$  are naturally occurring compounds. Identified sources include ice algae, phytoplankton, and macroalgae [Gschwend *et al.*, 1985; Manley *et al.*, 1992; Sturges *et al.*, 1993; Moore and Tokarczyk, 1993; Tokarczyk and Moore, 1994; Laturnus, 1995]. Reactions with OH [Mellouki *et al.*, 1992; Orkin *et al.*, 1997; Bilde *et al.*, 1998] and photolysis [Gillotay *et al.*, 1988; Moortgat *et al.*, 1993; Bilde *et al.*, 1998] represent the known atmospheric sinks. Evaluation of temporal trends in mixing ratios is not possible at this time due to the lack of sufficient data. Average tropospheric mixing ratios, lifetimes, and ODPs of the short-lived organic bromine compounds are found in Table 1.

### 3. Methods

Whole air samples were collected by the National Center for Atmospheric Research (NCAR) Whole Air Sampler on board the NASA ER-2 aircraft during the STRAT campaign in 1996. The STRAT samples were collected between the tropics and about 60°N from near the surface to 21 km (Figure 1a). The Whole Air Sampler [Heidt *et al.*, 1989; Schauffler *et al.*, 1993; Daniel *et al.*, 1996] was modified to increase the number of sample canisters from 29 to 49. The sampler included a four-stage metal bellows pump, a stainless steel manifold, an electronics control package, and the 49 electropolished stainless steel canisters. The canisters were filled to ~3 standard atmospheres (~40 psi) and returned to the laboratory for analysis. The filling time for each canister was about 10 s at 8 km to 3.5–4 min at 20 km. These short fill times



**Figure 1.** Distribution by latitude and altitude of samples collected during (a) STRAT and (b) PEM Tropics.

ensure a negligible source of uncertainty from inhomogeneities in halocarbon abundance during the filling of a given canister. Canisters were analyzed within 2–14 days after sample collection.

Whole air samples from PEM Tropics were collected by the University of California, Irvine (UCI), whole air sampling systems on board the NASA P3 and DC8 aircraft. The UCI PEM Tropics samples were collected in the Pacific region from 73°S to 45°N and from near the surface to ~12 km (Figure 1b). The UCI system includes a metal bellows pump, a stainless steel manifold, and electropolished stainless steel canisters [D.R. Blake *et al.*, 1996]. A maximum of 168 samples were collected per flight. The canisters were filled to ~40 psi and analyzed at UCI for a variety of hydrocarbons and halocarbons. A subsample of the total number of canisters was then shipped to NCAR for analysis of halocarbons and other compounds. The UCI canisters were analyzed at UCI within 2–10 days after sample collection and were analyzed at NCAR within 30–60 days after sample collection.

At NCAR the halons,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_2\text{Cl}$ , and  $\text{CHBr}_3$ , were analyzed using gas chromatography with mass selective detection (GC/MS). Approximately 500 mL of sample was concentrated at -185°C in a glass-bead-packed nickel sample loop. The GC column was a 30-m fused silica column with a 0.25-mm ID and a 1.0 µm thick bonded nonpolar silicone phase (J&W Scientific DB-1). The temperature profile was -65°C for 1 min, 8°C/min to 120°C, and 70°C/min to 175°C for 2.1 min. Total analysis time was 27 min. The GC was a Hewlett Packard

5890, and the detector was a Hewlett Packard 5971A mass selective detector operated in the single-ion mode with electron impact ionization. Under these sampling conditions the detection limits were <0.5 ppt for  $\text{CBrF}_3$ , <0.05 ppt for  $\text{CBrClF}_2$  and  $\text{CBrF}_2\text{CBrF}_2$ , <0.1 ppt for  $\text{CH}_3\text{Br}$ , <0.02 ppt for  $\text{CH}_2\text{Br}_2$ , <0.04 ppt for  $\text{CHBr}_2\text{Cl}$ , and <0.05 ppt for  $\text{CHBr}_3$ .

$\text{CH}_2\text{BrCl}$  and  $\text{CHBrCl}_2$  were analyzed using gas chromatography with negative ion chemical ionization detection (GC/NICI). The GC was a Hewlett Packard 5890 Series II, and the detector was a VG Instruments Trio 1000. Approximately 100 mL of sample was concentrated at  $-185^\circ\text{C}$  in a glass-bead-packed nickel sample loop. The GC column and temperature program was comparable to that used for the GC/MSD. Under these sampling conditions the detection limits were <0.01 ppt for  $\text{CH}_2\text{BrCl}$  and  $\text{CHBrCl}_2$ .

The UCI analytical system for all halogenated organic compounds was a Hewlett Packard 5890 Series II GC with an electron capture detector (GC/ECD). Approximately  $1500\text{ cm}^3$  of sample was concentrated at  $-196^\circ\text{C}$  in a glass-bead-packed stainless steel sample loop. The sample was divided into six portions, three for flame ionization detection and three for GC/ECD analysis. Total analysis time was 20 min. Under these sampling conditions the detection limits were <0.5 ppt for  $\text{CBrF}_3$ , <0.03 ppt for  $\text{CBrClF}_2$  and  $\text{CBrF}_2\text{CBrF}_2$ , <0.2 ppt for  $\text{CH}_3\text{Br}$ , <0.03 ppt for  $\text{CH}_2\text{Br}_2$ , <0.04 ppt for  $\text{CHBr}_2\text{Cl}$ , <0.05 ppt for  $\text{CHBr}_3$ , and <0.01 ppt for  $\text{CH}_2\text{BrCl}$  and  $\text{CHBrCl}_2$ . Details of the UCI analytical system, standards, and calibrations have been previously reported [Blake *et al.*, 1992, 1994, 1996].

Mixing ratios for the NCAR samples were calculated based on secondary standards of remote continental tropospheric air collected at Niwot Ridge, Colorado, in September 1993. The secondary standards were calibrated against primary standards prepared in this laboratory from pure compounds and from dilutions of commercially prepared multicomponent standards. The secondary standards were run periodically against each other during the STRAT sampling period to check for drift of individual components over time. Drift was noted for  $\text{CH}_3\text{Br}$  ( $\sim 0.5$  ppt/yr in 1996) in one of the cylinders and was taken into account in calculations of the mixing ratios. Primary standards prepared in this laboratory were of the order of 50 ppb for  $\text{CBrClF}_2$  and 50 ppb to 10 ppt for  $\text{CBrF}_3$ . The manufacturer-certified multicomponent primary standard used for  $\text{CH}_3\text{Br}$  calibration was 18 ppb. The multicomponent standards used for  $\text{CBrF}_2\text{CBrF}_2$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ ,  $\text{CH}_2\text{BrCl}$ ,  $\text{CHBrCl}_2$ , and  $\text{CHBr}_2\text{Cl}$  were not certified and were nominally listed as 100 ppb. These standards were calibrated in this laboratory using gas chromatography with atomic emission detection (GC/AED) based on carbon and halogen responses relative to National Institute of Standards and Technology (NIST) certified standards. The operating principle of the AED is that molecules eluting from the chromatographic column are excited to their constituent atomic species in a plasma and the specific atomic emission of the individual elements is detected with a diode array spectrometer. The response to the elemental atomic emission is independent of the molecular source of the constituent atom and is proportional to the number of atoms in the molecule. For this reason, a certified hydrocarbon standard may be used to calibrate halocarbon mixtures. This equivalence of response between different classes of compounds is not seen in any other detector. We evaluated the calibration on a certified NIST Standard Reference Material 1813 cylinder containing four halocarbons ( $\sim 250$  ppb each) using a certified NIST butane/benzene mixture

(10 ppb each). The calibration was within the stated values, so we subsequently used both standards to calibrate the commercially prepared multicomponent halocarbon mixtures. The analytical procedure for the GC/AED involved introduction of  $\sim 1$  L of the standard onto a Supelco Carbotrap 200 adsorbent cartridge (80 mg glass beads, 170 mg Carbotrap B, 350 mg Carbosieve S III) followed by thermal desorption to a cryofocusing trap prior to introduction onto the GC column. The precision of the technique as described was  $\sim 3\%$ ; this variability was primarily a result of the precision of the pressure transducer used in the volume measurement. The accuracy of the NIST hydrocarbon standard was  $<1\%$ , and the NIST halocarbon standard was  $\pm 1\%$ . The ppb level primary halocarbon standards were diluted to ppt levels by both flow and static dilution systems for calibrating the secondary standards. Linearity of the instruments was evaluated using flow dilutions of ambient air samples down to 10–20% of ambient. Corrections for nonlinear effects were not required for any of the compounds reported here.

The uncertainties in our measurements result from the following: instrument precision, sampling precision, standards calibration precision, and accuracy of the standards. To evaluate instrument precision, we determine the precision on repeated analysis of the working standard. We were unable to analyze a given canister enough times to evaluate instrument precision on ambient samples; therefore, for uncertainty calculations we assumed the precision from the working standard was equivalent to the precision from the samples. The GC/NICI response drifted by a variable amount during each day (up to  $\sim 20\%$ ), so all measurements were corrected by interpolating between standard runs. Two samples were analyzed between each standard run. To evaluate the sampling precision, we compare samples collected in the same region consecutively, or nearly consecutively. The precision of the GC systems for repeat runs of the secondary standard for each compound and the sampling precision from analysis of multiple canisters are listed in Table 2. Also listed in Table 2 are the total uncertainties for each compound. These values were calculated by taking the square root of the sum of the squares of the percent uncertainties in standard preparation or dilution, the standard deviation in percent for repeated runs of the standards and samples, the standard deviation in percent for analysis of multiple canisters, and the standard deviation in percent of the standard mixing ratios.

The precision from multiple canisters also provided indirect information on the stability of a given trace gas in the canisters. Generally, compounds with low or inconsistent stability in the canisters exhibited significant variability and low mixing ratios relative to previously measured values. The halons and  $\text{CH}_3\text{Br}$  showed excellent reproducibility in multiple canisters (Table 2). The remaining gases showed higher variability in the multiple canisters; however, the magnitude of the variability was consistent with the total uncertainties for each gas. Higher uncertainties are not unusual for short-lived compounds at sub-ppt levels. The tropospheric mixing ratios of the short-lived species were all within the range of previous measurements as discussed below. An additional indication of canister stability was obtained from the few ER-2 canisters that were reanalyzed. Six samples collected during STRAT were reanalyzed 1–4 weeks after the initial analysis and showed variability consistent with the values presented in Table 2. Adequate stability of the trace gases in the UCI canisters was also indicated by direct comparison of measurements from both groups on the same canisters during PEM Tropics. As mentioned above, the UCI and

**Table 2.** Variability of Daily Averages of the Working Standard and of Single Analyses of Multiple Canisters Collected at Similar Altitudes and Latitudes

Sample Information	Mean s.d, CV									
		CH <sub>3</sub> Br	CBrF <sub>3</sub>	CBrClF <sub>2</sub>	C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub>	CH <sub>2</sub> Br <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	CH <sub>2</sub> BrCl	CHBrCl <sub>2</sub>
CV for daily standard, %		1.0	3.0	1.5	4.0	2.5	2.2	4.4	7.0	6.8
Total Uncertainty, %		3.5	6.0	4.0	7.0	11.0	15.0	15.0	20.0	20.0
Jan. 26, 1996, n=8, 17.7–18.1 km, 36°N	Mean	5.63	1.64	1.67	0.23	0.20	0	0	0.06	0.008
	s.d.	0.10	0.06	0.05	0.01	0.01	0	0	0.01	0.002
	CV	1.8	3.4	3.1	3.7	6.0			12.0	23.9
Jan 29, 1996, n=14, 11.5–12.7 km, 37°N	Mean	10.39	2.21	3.35	0.46	0.93	0.14	0.47	0.18	0.10
	s.d.	0.14	0.05	0.05	0.02	0.10	0.02	0.13	0.03	0.02
	CV	1.3	2.1	1.5	4.0%	10.4	16.1	28.6	13.9	23.0
Feb. 2, 1996, n=8, 10.8 km, 28°N	Mean	10.55	2.22	3.40	0.46	0.96	0.11	0.27	0.21	0.11
	s.d.	0.09	0.06	0.04	0.02	0.04	0.03	0.06	0.02	0.02
	CV	0.9	2.6	1.2	3.6%	4.0	23.3	23.4	7.5	20.5
Feb. 2, 1996, n=5, 11.4 km, 36°N	Mean	10.48	2.23	3.39	0.47	0.93	0.10	0.28	0.19	0.10
	s.d.	0.14	0.05	0.05	0.02	0.08	0.05	0.19	0.03	0.02
	CV	1.3	2.2	1.6	3.3%	8.8	46.1	65.8	13.4	20.9
Feb. 2, 1996, n=8, 12 km, 36°N	Mean	10.14	2.28	3.34	0.46	0.77	0	0	0.16	0.06
	s.d.	0.07	0.06	0.04	0.004	0.03	0	0	0.02	0.01
	CV	0.7	2.7	1.2	1.0%	4.3			10.1	19.2
Feb. 12, 1996, n=3, 18.7 km, 21°N	Mean	6.75	1.76	2.12	0.29	0.23	0	0	0.05	0
	s.d.	0.02	0.02	0.02	0.01	0.05	0	0	0.01	0
	CV	0.4	1.4	0.8	2.0%	21.6			19.7	
Feb. 15, 1996, n=4, 19.2 km, 24°N	Mean	5.05	1.51	1.52	0.22	0.09	0	0	0.04	0
	s.d.	0.10	0.09	0.03	0.01	0.04	0	0	0.01	0
	CV	2.0	5.8	2.1	3.7%	40.8			21.1	

CV, coefficient of variation, equals s.d. (standard deviation)/mean. CV units are percent. Mean and SD units are ppt. Total uncertainty is the square root of the sum of the squares of the percent uncertainties in standard calibrations and the standard deviation in percent for repeat runs of the standards, individual samples, and canisters collected at the same altitude.

NCAR analyses were carried out 2–14 days and 30–60 days, respectively after sampling. The following values represent the percent variability in the ratio of NCAR/UCI measurements from ~600 samples: CBrF<sub>3</sub>, 6.9%; CBrClF<sub>2</sub>, 2.3%; CBrF<sub>2</sub>CBrF<sub>2</sub>, 7.0%; CH<sub>3</sub>Br, 6.0%; CH<sub>2</sub>Br<sub>2</sub>, 9.5%; CHBr<sub>3</sub>, 32.6%; CHBrCl<sub>2</sub>, 49.0%; CHBr<sub>2</sub>Cl, 39.5%. The variability in the latter two compounds is not surprising given their tropospheric mixing ratios are ~0.15 ppt.

Our primary mechanism for evaluation of the NCAR calibration scales relative to those of other laboratories has been by comparison of measurements from similar samples, although we have participated in a number of informal intercalibrations through exchange of primary and secondary standards. Our calibration scales for the three halons and CH<sub>3</sub>Br are in good agreement with NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) and are within 3% for CBrClF<sub>2</sub> and CBrF<sub>2</sub>CBrF<sub>2</sub> and within 5% for CBrF<sub>3</sub> and CH<sub>3</sub>Br. We have no direct comparisons for the other compounds.

The NCAR and UCI calibration scales for the halons agree to within <2%. For the PEM Tropics samples the NCAR values for CBrF<sub>3</sub> were more scattered than the UCI values, while the UCI values for CBrF<sub>2</sub>CBrF<sub>2</sub> were more scattered than the NCAR values. Differences in the chromatography and detectors between the two analytical systems account for the differences in

variability. The only other compound with an independent calibration scale between the two laboratories is CH<sub>3</sub>Br. For this compound the NCAR values are generally ~9% larger than the UCI values. We are currently evaluating possible reasons for this discrepancy. The UCI values for the remaining organic bromine compounds were calibrated based on the NCAR calibration scale. The UCI values for CHBr<sub>3</sub> agree well with those of NCAR for measurements on the same canisters. However, the UCI values for CH<sub>2</sub>Br<sub>2</sub>, CHBrCl<sub>2</sub>, and CHBr<sub>2</sub>Cl are somewhat lower than the NCAR values. The nature of the correlations suggests possible nonlinearity in the ECD response to these compounds. We are in the process of investigating this possibility.

The ER-2 flights during the STRAT campaign were based out of Moffet Field, California (37°N, 122°W), and Barbers Point, Hawaii (19°N, 156°W). As a result, most of our upper troposphere samples (from descents and dives) were near these locations (Figure 1a). Therefore we have combined our upper troposphere measurements into three latitude regions for presentation in this paper. The three regions are 2°S–6°N, where samples were collected during dives at the tropical tropopause; 21–24°N from flights out of Hawaii; and 36–41°N from flights out of Moffet Field. We averaged the PEM Tropics data (Figure 1b) over these same latitude regions for comparison with the STRAT data. We combined the PEM Tropics data with the

**Table 3a.** Averaged Tropospheric Mixing Ratios of All Species and Total Organic Bromine from the STRAT Measurements During the Three Deployments

	CH <sub>3</sub> Br				CBrF <sub>3</sub>				CBrClF <sub>2</sub>			
	Jan.	July	Dec.	All	Jan.	July	Dec.	All	Jan.	July	Dec.	All
1°S–7°N mean	9.67	9.36	na	9.45	2.28	2.21	2.53	2.34	3.32	3.40	3.45	3.41
s.d.	0.10	0.43		0.39	0.07	0.18	0.12	0.21	0.05	0.07	0.04	0.07
CV, %	1.0	4.6		4.1	3.1	8.1	4.7	9.0	1.5	2.1	1.2	2.1
21–24°N mean	9.83	9.67	9.21	9.79	2.28	2.17	2.50	2.25	3.40	3.48	3.47	3.45
s.d.	0.17	0.31	0.57	0.27	0.12	0.10	0.11	0.14	0.06	0.06	0.04	0.07
CV, %	1.8	3.2	6.1	2.8	5.3	4.8	4.5	6.2	1.6	1.6	1.3	2.0
36–41°N mean	10.35	10.35	9.93	10.31	2.23	2.36	2.53	2.36	3.37	3.48	3.62	3.48
s.d.	0.37	0.36	0.50	0.39	0.06	0.15	0.21	0.19	0.06	0.06	0.06	0.12
CV, %	3.6	3.5	5.1	3.8	2.7	6.2	8.2	8.1	1.8	1.8	1.7	3.6
All troposphere samples												
Mean	10.09	9.85	9.69	9.95	2.26	2.23	2.52	2.30	3.38	3.48	3.57	3.46
s.d.	0.41	0.45	0.61	0.46	0.09	0.15	0.18	0.18	0.06	0.06	0.09	0.10
CV, %	4.1	4.6	6.3	4.6	4.0	6.7	7.1	7.8	1.8	1.7	2.5	2.9
Contribution to total organic bromine, %	51.7	52.3	50.6	52.1	11.6	11.8	13.2	12.0	17.3	18.5	18.6	18.1

	C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub>				CH <sub>2</sub> Br <sub>2</sub>				CHBr <sub>2</sub> Cl			
	Jan.	July	Dec.	All	Jan.	July	Dec.	All	Jan.	July	Dec.	All
1°S–7°N mean	0.45	0.44	0.44	0.44	0.85	0.48	0.36	0.49	0.06	0.00	0.00	
s.d.	0.02	0.02	0.03	0.02	0.02	0.08	0.14	0.21	0.01	0.00	0.00	
CV, %	3.8	4.5	6.4	4.5	2.4	16.7	38.9	42.9	16.1	0.0	0.0	
21–24°N mean	0.45	0.46	0.44	0.45	0.87	0.79	0.38	0.76	0.08	0.08	0.05	0.08
s.d.	0.02	0.02	0.02	0.02	0.12	0.10	0.22	0.19	0.03	0.08	0.03	0.03
CV, %	3.9	3.6	5.6	4.4	13.3	12.2	56.7	25.0	35.3	29.6	49.5	32.0
36–41°N mean	0.46	0.45	0.46	0.45	0.89	0.73	0.88	0.80	0.11	0.09	0.10	0.10
s.d.	0.02	0.02	0.02	0.02	0.19	0.12	0.04	0.21	0.04	0.01	0.03	0.04
CV, %	4.6	3.4	3.7	4.4	21.7	16.1	4.9	26.3	38.0	15.2	28.4	37.9
All troposphere samples												
Mean	0.45	0.45	0.46	0.45	0.87	0.75	0.79	0.76	0.10	0.08	0.09	0.09
s.d.	0.02	0.02	0.02	0.02	0.16	0.13	0.18	0.21	0.04	0.02	0.04	0.03
CV, %	4.4	3.7	3.9	4.4	18.4	16.8	23.2	27.6	40.0	25.0	38.5	33.3
Contribution to total organic bromine, %	4.6	4.8	4.8	4.7	8.9	8.0	8.2	8.0	1.0	0.8	0.9	0.9

STRAT July/August data to evaluate vertical distributions in the troposphere and lower stratosphere. For these profiles we used NCAR measurements from the PEM Tropics samples for all species except CBrF<sub>3</sub>. We use the UCI CBrF<sub>3</sub> measurements because the two calibration scales are equivalent and the UCI measurements are less variable. We use the UCI PEM Tropics measurements of the short-lived species when we discuss the relative vertical distributions from all PEM Tropics samples combined because it is a substantially larger data set relative to NCARs. Tropospheric samples were defined as samples with CCl<sub>3</sub>F mixing ratios of 267 ppt or greater.

#### 4. Results and Discussion

Averaged tropospheric mixing ratios of all species and total organic bromine from the STRAT measurements for the three

sampling periods and the three latitude groups are presented in Tables 3a and 3b. Significant seasonal variations were not observed in any of the measured species in the upper troposphere, although a number of the compounds have shown some seasonality at the surface [Cicerone *et al.*, 1988; Yokouchi *et al.*, 1996; Atlas and Ridley, 1996]. Table 4 shows the comparison of the July STRAT measurements with those of PEM Tropics for the three latitude groups. Sections 4.1–4.5 discuss the results for each compound and for total organic bromine.

##### 4.1. Halons 1301, 2402, and 1211

The mean CBrF<sub>3</sub> and CBrF<sub>2</sub>CBrF<sub>2</sub> mixing ratios for all STRAT troposphere samples were 2.30±0.18 ppt and 0.45±0.02 ppt (Table 3a). These values were consistent with surface measurements from Butler *et al.* [1998] of 2.3 ppt and 0.45 ppt for CBrF<sub>3</sub> and CBrF<sub>2</sub>CBrF<sub>2</sub>, respectively. The growth rates of

Table 3a. cont.

	CHBr <sub>3</sub>				CH <sub>2</sub> BrCl				CHBrCl <sub>2</sub>			
	Jan.	July	Dec.	All	Jan.	July	Dec.	All	Jan.	July	Dec.	All
1°S-7°N mean	0.10	0.00	0.00		0.16	0.13	0.09	0.12	0.07	0.01	0.01	0.02
s.d.	0.03	0.00	0.00		0.03	0.02	0.03	0.03	0.02	0.01	0.01	0.02
CV, %	30.0	0.0	0.0		18.8	15.4	33.3	25.0	28.6	100	100	100
21-24°N mean	0.10	0.13	0.00	0.12	0.18	0.17	0.10	0.16	0.07	0.08	0.02	0.07
s.d.	0.04	0.06	0.00	0.05	0.03	0.01	0.04	0.03	0.03	0.02	0.02	0.03
CV, %	41.0	43.0	0.0	41.7	14.8	5.9	40.3	18.8	46.0	22.4	100	42.9
36-41°N mean	0.33	0.21	0.20	0.26	0.18	0.17	0.08	0.16	0.08	0.07	0.07	0.07
s.d.	0.22	0.07	0.17	0.19	0.04	0.02	0.08	0.05	0.04	0.04	0.07	0.04
CV, %	67.2	31.1	86.3	73.1	20.4	11.8	100	31.3	53.4	53.1	100	57.1
All troposphere samples												
Mean	0.23	0.16	0.18	0.19	0.18	0.16	0.11	0.16	0.07	0.07	0.05	0.07
s.d.	0.20	0.07	0.17	0.15	0.03	0.02	0.08	0.04	0.04	0.03	0.05	0.03
CV, %	87.6	43.8	91.0	78.9	17.7	10.3	69.5	25.0	51.0	39.7	100	42.9
Contribution to total organic bromine, %	3.5	2.5	2.8	3.0	0.9	0.8	0.6	0.8	0.4	0.4	0.3	0.4

Total Organic Bromine				
	Jan.	July	Dec.	All
1°S-7°N mean	18.4 (18.5)	17.0 (17.0)		17.4 (17.2)
s.d.	0.3	0.7		0.1
CV, %	1.6	4.1		0.5
21-24°N mean	18.6 (18.8)	18.4 (18.6)	17.6 (17.1)	18.5 (18.7)
s.d.	0.6	0.4	0.6	0.5
CV, %	3.5	2.1	3.4	2.9
36-41°N mean	19.5 (20.1)	19.2 (19.6)	19.5 (19.7)	19.5 (19.9)
s.d.	1.6	1.1	1.8	1.4
CV, %	8.1	5.5	9.4	7.3
All troposphere samples				
Mean	19.1 (19.5)	18.5 (18.8)	18.8 (19.6)	18.8 (19.1)
s.d.	1.3	0.8	1.7	1.2
CV, %	6.8	4.3	9.2	6.2

All represents the averages over the three sampling periods by latitude group. All troposphere samples and contribution to total organic bromine represent the averages over the three latitude groups by sampling period. The total organic bromine values are averages of the total organic bromine in samples from each group. The total organic values in parentheses are the sum of the averages presented in the table of individual species. na, not available; units are ppt. Table 3b contains sample numbers, altitude averages, and altitude ranges for the three latitude groups.

Table 3b. Number of Samples, Altitude Range, and Altitude Averages for Each Sampling Period and Latitude Group

Sampling Period	n	Altitude Range, km	Altitude Mean, km
1°S-7°N			
Jan.	4	16.4-17.3	16.9 ± 2%
July	8	15.7-17.5	16.4 ± 4%
Dec.	5	15.7-17.2	16.3 ± 4%
21-24°N			
Jan.	29	11.3-17.4	14.9 ± 14%
July	50	8.7-13.3	12.2 ± 8%
Dec.	9	11.6-14.8	13.2 ± 12%
36-41°N			
Jan.	37	9.5-15.5	12.1 ± 10%
July	23	9.4-14.7	12.0 ± 14%
Dec.	30	11.5-13.3	10.7 ± 18%

these species for this time period were relatively low,  $0.044 \pm 0.011$  ppt/yr for CBrF<sub>3</sub> and  $0.009 \pm 0.001$  ppt/yr for CBrF<sub>2</sub>CBrF<sub>2</sub> [Butler *et al.*, 1998]. These values were within our precision for the STRAT samples so we were unable to measure an increase in either compound during 1996. The latitudinal distribution of a given species depends on the lifetime, the source and sink locations and strengths, and the interhemispheric exchange time. Anthropogenic species with larger production rates in the Northern Hemisphere often show north/south latitudinal gradients in mixing ratios, with larger values in the north. For these species the magnitude of the north/south gradient is inversely related to atmospheric lifetime because the interhemispheric exchange time of about a year allows for long-term mixing between the hemispheres. We observed a small north/south latitudinal gradient for CBrF<sub>2</sub>CBrF<sub>2</sub> of ~0.01 ppt in



Table 4. Comparison of NCAR and UCI Analyses on Identical Samples Collected During PEM Tropics

	CH <sub>3</sub> Br		CBrF <sub>3</sub>		CBrClF <sub>2</sub>		C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub>		CH <sub>2</sub> Br <sub>2</sub>		CHBrCl <sub>2</sub>		CHBrF <sub>2</sub>		CHBr <sub>3</sub>	
	NCAR	UCI	NCAR	UCI	NCAR	UCI	NCAR	UCI	NCAR	UCI	NCAR	UCI	NCAR	UCI	NCAR	UCI
PT all mean	9.66	8.83	2.23	2.30	3.39	3.41	0.45	0.48	1.08	0.94	0.23	0.14	0.16	0.13	1.21	1.13
s.d.	0.64	0.56	0.15	0.05	0.06	0.05	0.02	0.03	0.25	0.17	0.12	0.07	0.04	0.05	0.82	0.82
PT >2 km mean	9.78	8.94	2.23	2.30	3.42	3.41	0.45	0.50	0.91	0.82	0.15	0.11	0.13	0.11	0.63	0.53
s.d.	0.54	0.49	0.16	0.04	0.05	0.05	0.01	0.03	0.08	0.08	0.04	0.05	0.02	0.05	0.26	0.20
STRAT mean	9.51		2.27		3.44		0.44		0.52		0.00		0.02		0.00	
s.d.	0.22		0.18		0.07		0.01		0.05		0.01		0.01			
PT >2 km mean	11.3	10.30	2.28	2.35	3.57	3.49	0.46	0.49	0.82	0.75	0.14	0.10	0.14	0.09	0.41	0.47
s.d.	0.57	0.36	0.24	0.03	0.05	0.07	0.03	0.02	0.05	0.07	0.03	0.04	0.03	0.04	0.16	0.15
STRAT mean	9.67		2.17		3.48		0.46		0.79		0.08		0.08		0.13	
s.d.	0.31		0.10		0.06		0.02		0.10		0.02		0.02		0.06	
PT >2 km mean	11.5	11.23	2.12	2.32	3.58	3.57	0.48	0.49	0.78	0.79	0.13	0.08	0.13	0.05	0.34	0.35
s.d.	0.84	0.78	0.24	0.04	0.05	0.05	0.03	0.01	0.09	0.03	0.03	0.03	0.02	0.02	0.11	0.08
STRAT mean	10.35		2.36		3.48		0.45		0.73		0.09		0.07		0.21	
s.d.	0.36		0.15		0.06		0.02		0.12		0.01		0.04		0.07	

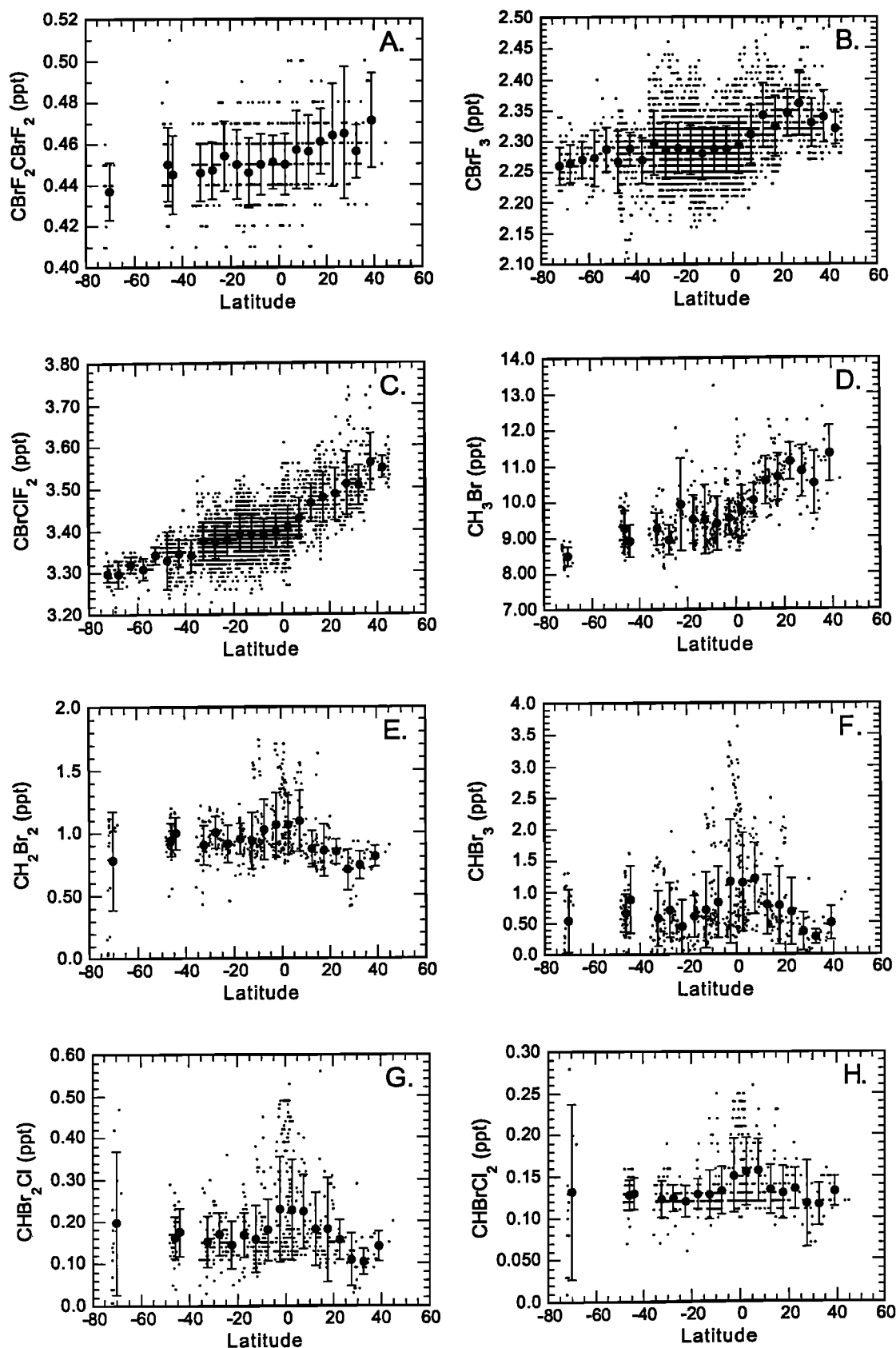
Upper troposphere STRAT values are included for comparison with PEM Tropics. All units are ppt. PT is PEM Tropics and s.d. is standard deviation. CH<sub>2</sub>BrCl was not measured in the PEM Tropics samples.

PEM Tropics samples analyzed by NCAR (Figure 2a). We also observed a slight latitudinal gradient for CBrF<sub>3</sub> of about 0.05 ppt when all the PEM Tropics samples were plotted by latitude (Figure 2b). The small latitudinal gradients for CBrF<sub>2</sub>CBrF<sub>2</sub> and CBrF<sub>3</sub> were not statistically significant; however, they were consistent with their annual growth rate for this time period [Butler *et al.*, 1998]. There was no significant difference between the PEM Tropics mixing ratios and the upper troposphere STRAT mixing ratios of CBrF<sub>3</sub> and CBrF<sub>2</sub>CBrF<sub>2</sub> with the exception of smaller CBrF<sub>3</sub> in the STRAT 21–24°N samples (relative to the UCI CBrF<sub>3</sub> values) (Table 4). These samples were primarily from a single flight, which showed slightly smaller mixing ratios of a number of the chlorinated organic species.

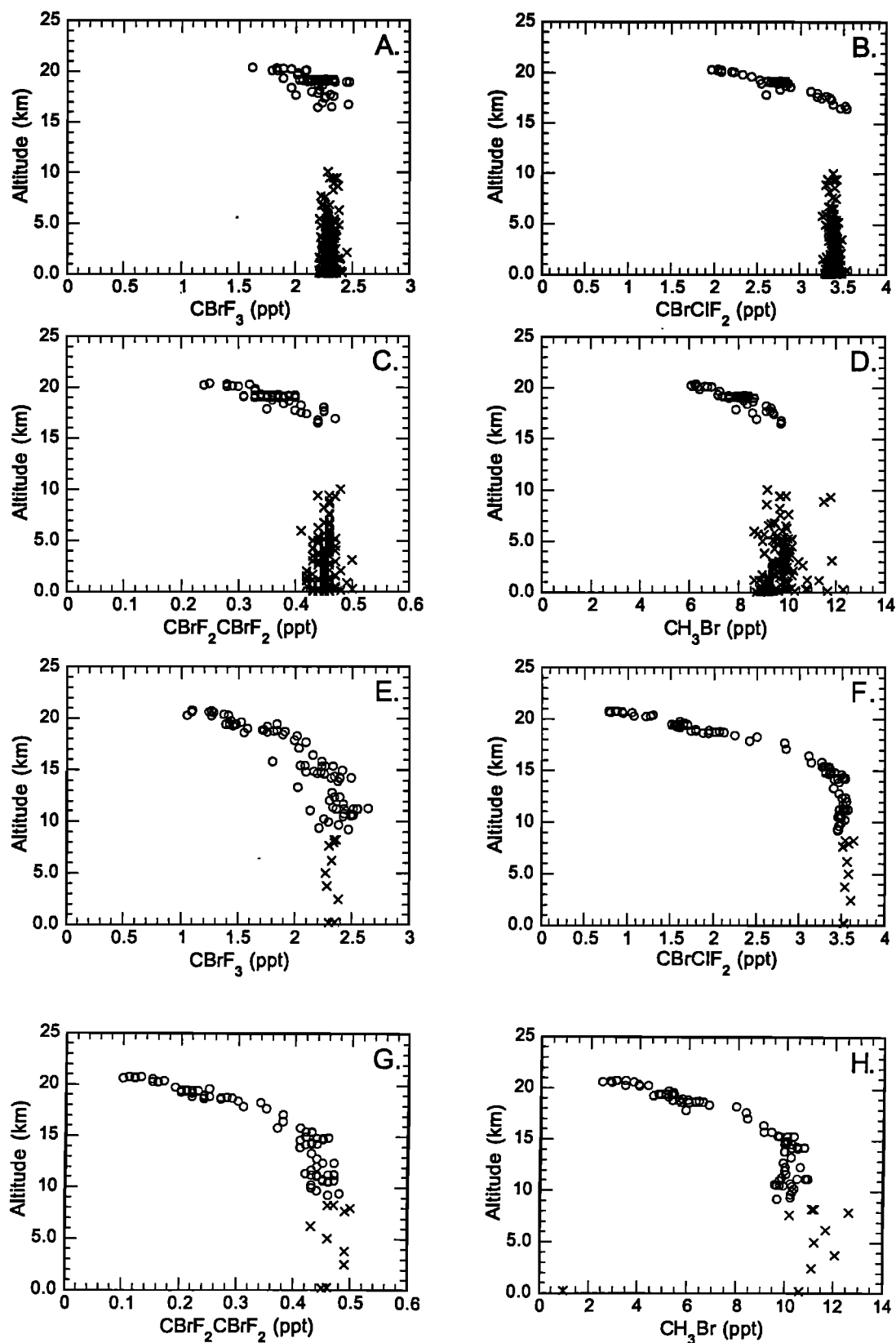
The mean CBrClF<sub>2</sub> mixing ratio for all STRAT December troposphere samples was 3.57±0.09 ppt (Table 3a) which was consistent with 3.5 ppt from surface samples at the end of 1996 [Butler *et al.*, 1998]. The measured increase in CBrClF<sub>2</sub> mixing ratios between January/February 1996 and December 1996 (3.38–3.57 ppt) from the STRAT samples agreed well with the growth rate of 0.16±0.02 ppt for CBrClF<sub>2</sub> during 1996 reported by Butler *et al.* [1998]. The north/south latitudinal gradient for CBrClF<sub>2</sub> was about 0.20 ppt (Figure 2c), which was also consistent with the annual growth rate. The latitudinal distribution from the STRAT samples at the tropics and 21–24°N were in excellent agreement with the PEM Tropics samples (Table 4). The 36–41°N STRAT values were somewhat smaller than the corresponding values from PEM Tropics; however, as the standard deviations overlap, the difference was not considered significant.

The tropical vertical distributions of CBrF<sub>3</sub>, CBrClF<sub>2</sub>, and CBrF<sub>2</sub>CBrF<sub>2</sub> are presented in Figures 3a, 3b, and 3c and include measurements from PEM Tropics and STRAT. Figures 3e, 3f, and 3g show the corresponding distributions in midlatitudes. The correspondence of upper troposphere measurements of the halons with those in the mid-lower troposphere and the surface were not unexpected given the relatively long tropospheric lifetimes of these species (Table 1).

Mixing ratios of the halons decreased above the tropopause, which was about 16–17 km in the tropics and about 11–14 km in midlatitudes during July. CBrF<sub>3</sub> mixing ratios decrease proportionately less, relative to troposphere values, than CBrF<sub>2</sub>CBrF<sub>2</sub> and CBrClF<sub>2</sub> in both the tropics and midlatitudes. In the tropics the mixing ratios of CBrF<sub>3</sub> decreased by ~25% at 20 km relative to tropospheric values, while CBrF<sub>2</sub>CBrF<sub>2</sub> and CBrClF<sub>2</sub> decreased by ~45%. In midlatitudes the mixing ratios of CBrF<sub>3</sub> decreased by 50% at 20 km, while CBrF<sub>2</sub>CBrF<sub>2</sub> and CBrClF<sub>2</sub> decreased by almost 80%. This is a result of the longer photochemical lifetime of CBrF<sub>3</sub> relative to CBrF<sub>2</sub>CBrF<sub>2</sub> and CBrClF<sub>2</sub>. The proportional loss and linearity of the correlation between the July/August STRAT measurements of CBrF<sub>2</sub>CBrF<sub>2</sub> and CBrClF<sub>2</sub> indicate a comparable stratospheric lifetime for the two species (Figure 4). This is consistent with previous model calculations of the stratospheric lifetimes of the two halons [Pyle *et al.*, 1992]. Relatively few studies are available for comparison of gradients in the lower stratosphere. The gradients measured during STRAT of CBrF<sub>3</sub> and CBrClF<sub>2</sub> above the tropopause in the tropics appeared to be larger than that observed by Lal *et al.* [1994] in India (17.5°N); however, the low number of data points from the balloon samples between the tropopause and 20 km makes direct comparison difficult. The midlatitude CBrF<sub>3</sub>



**Figure 2.** Latitudinal distributions of PEM Tropics samples averaged over 5° latitude bins of (a)  $\text{CBrF}_2\text{CBrF}_2$ , (b)  $\text{CBrF}_3$ , (c)  $\text{CBrClF}_2$ , (d)  $\text{CH}_3\text{Br}$ , (e)  $\text{CH}_2\text{Br}_2$ , (f)  $\text{CHBr}_3$ , (g)  $\text{CHBr}_2\text{Cl}$ , and (h)  $\text{CHBrCl}_2$ . Dots are individual data points. Solid circles are averages. Error bars represent one standard deviation.



**Figure 3.** Vertical distributions in the tropics from STRAT July/August (open circles), and PEM Tropics (crosses) of (a) CBrF<sub>3</sub>, (b) CBrClF<sub>2</sub>, (c) CBrF<sub>2</sub>CBrF<sub>2</sub>, (d) CH<sub>3</sub>Br, (i) CHBr<sub>3</sub>, and (j) CH<sub>2</sub>Br<sub>2</sub> and in midlatitudes of (e) CBrF<sub>3</sub>, (f) CBrClF<sub>2</sub>, (g) CBrF<sub>2</sub>CBrF<sub>2</sub>, (h) CH<sub>3</sub>Br, (k) CHBr<sub>3</sub>, and (l) CH<sub>2</sub>Br<sub>2</sub>.

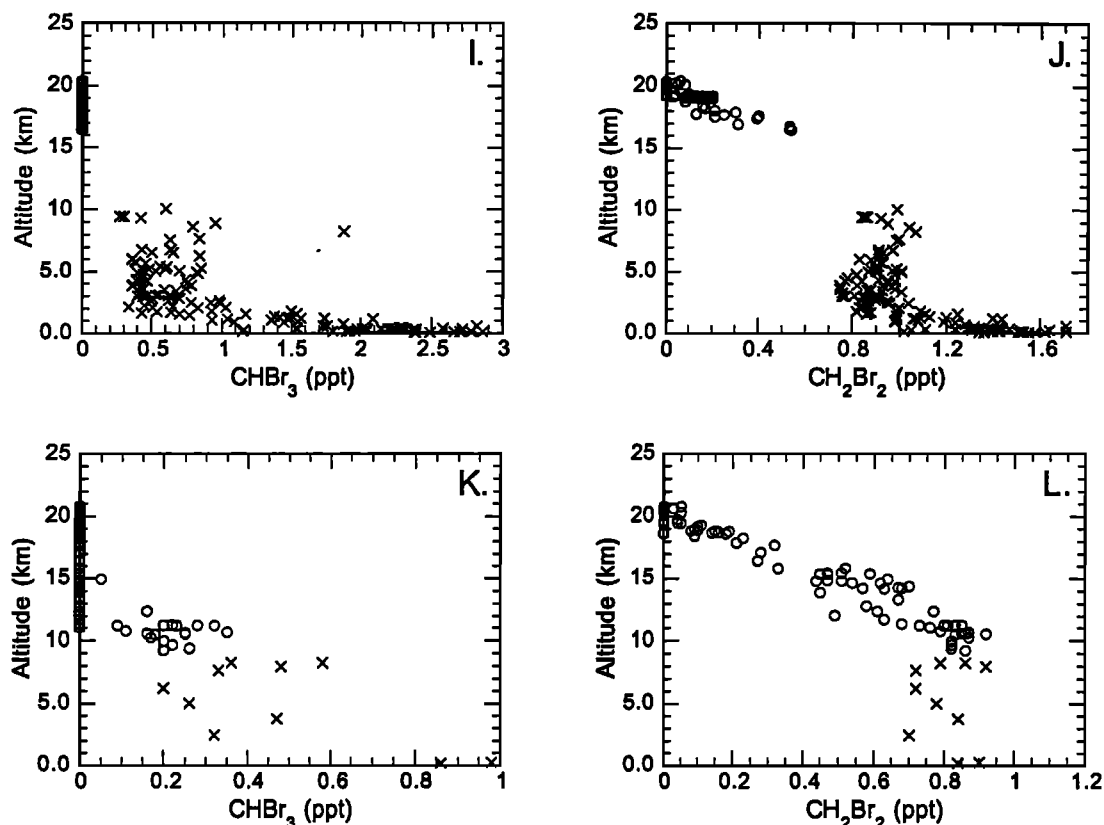
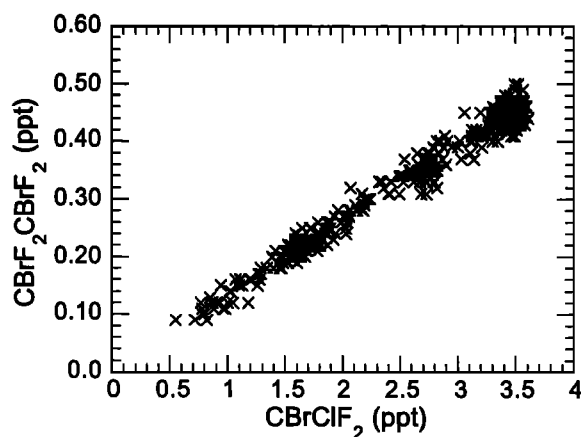
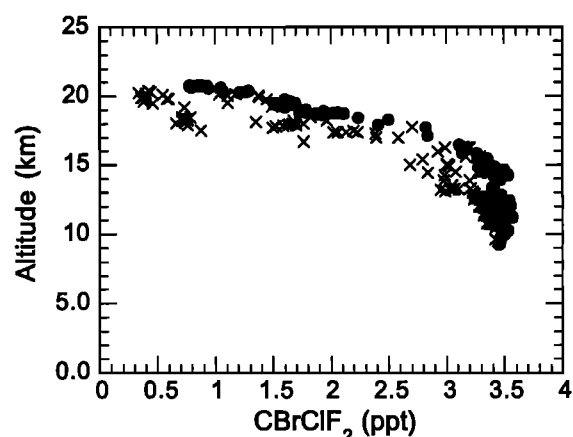


Figure 3. (continued)

gradient was somewhat less than the 80% decrease at 20 km measured by *Fabian et al.* [1996a,b] from balloon samples, whereas the CBrClF<sub>2</sub> gradient was equivalent. The gradients of CBrClF<sub>2</sub> above the tropopause in the tropics and midlatitudes were comparable to those observed by *Wamsley et al.* [1998] from aircraft measurements.

The winter midlatitude measured mixing ratios of the halons and CH<sub>3</sub>Br decreased from tropospheric values at lower altitudes than during summer, as shown in Figure 5 for CBrClF<sub>2</sub>. These

observations are presumably the result of greater downward transport in the lower stratosphere during the Northern Hemisphere winter [*Holton et al.*, 1995]. The greater downward transport resulted in lower tropopause altitudes in winter (~11.5 km) than in summer (~14 km) (B. Gary personal communication, 1996). The winter/summer differences in transport were reflected in the degree of loss of the halons between the tropopause and 20 km. The magnitude of the difference in loss in midlatitudes was ~11% for all three halons.

Figure 4. Correlation between CBrF<sub>2</sub>CBrF<sub>2</sub> and CBrClF<sub>2</sub> from July/August STRAT samples.Figure 5. Vertical distribution of CBrClF<sub>2</sub> in mid-latitudes from STRAT January (crosses) and July (solid circles) samples.

As with all brominated organic compounds, the mixing ratios at the tropical tropopause determine the amount of bromine from these source gases entering the stratosphere. For species such as  $\text{CBrClF}_2$ , which have increasing mixing ratios in the troposphere, the relationship between mixing ratios measured in the stratosphere at a given time and the amount of bromine released after entry into the stratosphere is dependent on the mixing ratio when the air parcel crossed the tropical tropopause. The difference between the time of the measurements and the time the air parcel crossed the tropical tropopause is referred to as the age of stratospheric air. The age may be determined from concurrent measurements of long-lived tracers, such as  $\text{SF}_6$ ,  $\text{CO}_2$ , or CFC 115 [Schmidt and Khedim, 1991; Pollock et al., 1992; Daniel et al., 1996; Harnish et al., 1996; Volk et al., 1997; Wamsley et al., 1998; Harnish et al., 1998]. These gases are useful as tracers of the age of air because they have a defined increasing growth rate in the troposphere and essentially no loss in the stratosphere. The STRAT measurements from July show an average  $\text{CBrClF}_2$  mixing ratio of  $3.40 \pm 0.07$  ppt at the tropical tropopause [Schauffler et al., 1998]. As mentioned previously, the magnitude of the north/south gradient of  $\text{CBrClF}_2$  is  $\sim 0.2$  ppt (Figure 2c), which is comparable to the annual growth. A typical time estimated for transport from the surface to the tropical tropopause is  $\sim 0.8$  year [Wamsley et al., 1998]. Of course, shorter times are possible during convective events so the range of transport times is of the order of hours to months. The latitudinal distribution and range of transport times imply that the 3.4 ppt measured at the tropical tropopause in July could have come from  $20^\circ\text{S}$ – $10^\circ\text{N}$  in July, from higher Northern Hemisphere latitudes about 9 months earlier, or some combination of the two. Although the potential error from these considerations in calculating the entry mixing ratio of  $\text{CBrClF}_2$  from age of air determinations is relatively small ( $<0.2$  ppt bromine), it may be important for other halogenated compounds with relatively large tropospheric growth rates and latitudinal gradients.

#### 4.2. Methyl Bromide

The tropospheric mixing ratios of  $\text{CH}_3\text{Br}$  showed a distinct latitudinal gradient during all three sampling periods of STRAT and during PEM Tropics (Tables 3 and 4 and Figure 2d). The north/south gradient of 1.18 observed during PEM Tropics was consistent with gradients measured at the surface [Lobert et al., 1995, 1996; Penkett et al., 1995] and from aircraft samples [Blake et al., 1997]. However, the STRAT mixing ratios were smaller and the gradient was less than those from PEM Tropics. The differences between the STRAT and PEM Tropics mixing ratios were not equivalent for the three latitude groups (Table 4). The tropics showed the least difference ( $\sim 3\%$ ), while the differences at  $21$ – $24^\circ\text{N}$  and  $36$ – $41^\circ\text{N}$  were  $\sim 14\%$  and  $\sim 10\%$ , respectively. A vertical gradient in  $\text{CH}_3\text{Br}$  in the troposphere is not unexpected, given the relatively short lifetime with respect to atmospheric loss ( $\sim 1.8$  years [Butler and Rodriguez, 1996]). However, the magnitude of the gradient may vary substantially, as observed here, and may even be reversed, i.e., larger mixing ratios with altitude, as a result of convective activity and large scale interhemispheric transport [Blake et al., 1997, also submitted manuscript, 1998]. The vertical gradient of  $\text{CH}_3\text{Br}$  at a given location is likely a result of local OH loss and regional and long-range transport, all of which may vary with altitude. The measurements presented here and those of Blake et al. [1997, submitted manuscript, 1998] indicate a likely range of 0–15% for the difference between surface and upper tropospheric mixing ratios of  $\text{CH}_3\text{Br}$ .

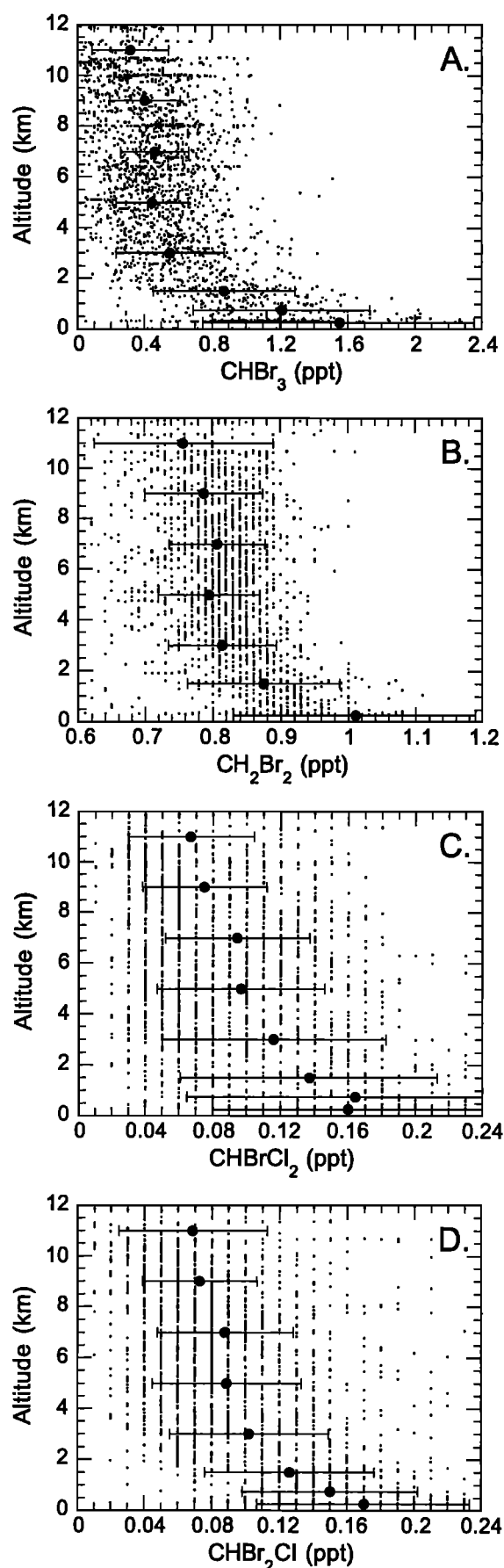


Figure 6. Vertical distributions of PEM Tropics samples of (a)  $\text{CHBr}_3$ , (b)  $\text{CH}_2\text{Br}_2$ , (c)  $\text{CHBrCl}_2$ , and (d)  $\text{CHBr}_2\text{Cl}$ .

The July mixing ratios of  $\text{CH}_3\text{Br}$  at 20 km in the tropics and midlatitudes were smaller by ~40% and ~70%, respectively relative to the tropopause values (Figures 3d and 3h). The January mixing ratios in the tropics and midlatitudes were smaller by ~30% and ~80%, respectively, relative to the tropopause values. The tropical gradients were larger than the gradient reported by Lal *et al.* [1994] from balloon samples at 17.5°N in 1990 but were equivalent to the gradient reported by Kourtidis *et al.* [1998] from balloon samples collected 3 years earlier at the same location. The observed gradients above the tropopause in this study imply a stratospheric loss with altitude somewhat smaller than  $\text{CBrF}_2\text{CBrF}_2$  and  $\text{CBrClF}_2$  but not as low as  $\text{CBrF}_3$ . This is consistent with a stratospheric lifetime longer than  $\text{CBrF}_2\text{CBrF}_2$  and  $\text{CBrClF}_2$  and shorter than  $\text{CBrF}_3$ .

#### 4.3. Short-Lived Brominated Organic Compounds

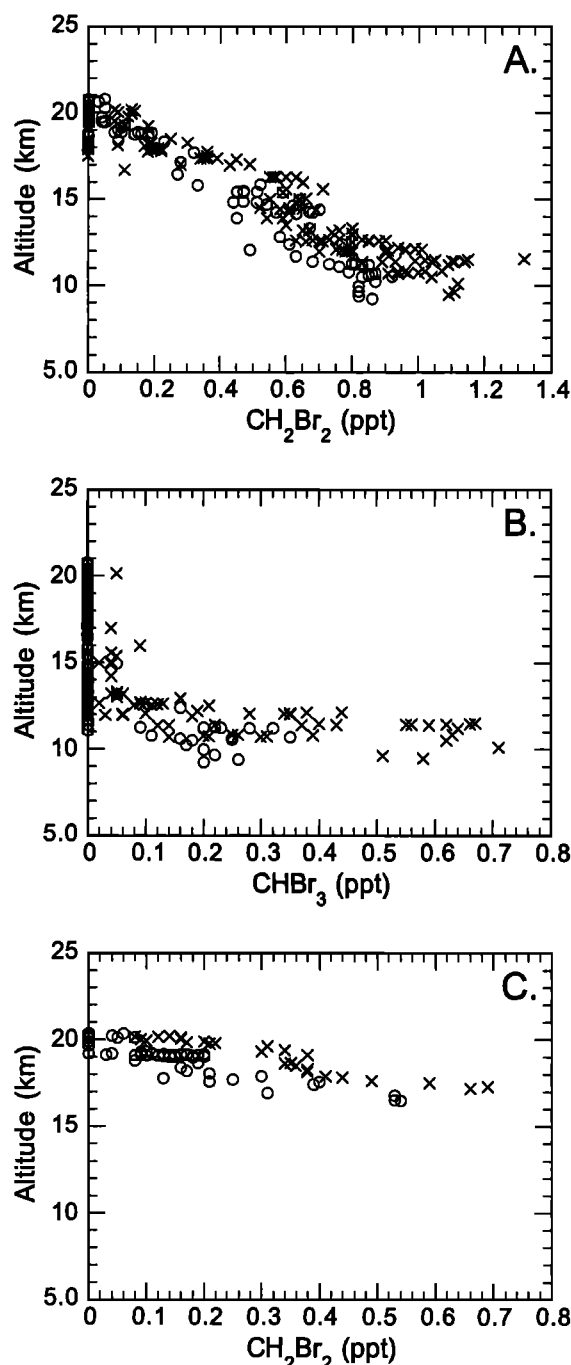
The short-lived brominated organic compounds,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ ,  $\text{CHBr}_2\text{Cl}$ , and  $\text{CHBrCl}_2$ , measured during PEM Tropics all showed a larger range of mixing ratios in the tropics relative to higher latitudes in either hemisphere (Figure 2e-2h). Interestingly,  $\text{CH}_2\text{Br}_2$  mixing ratios were somewhat larger in the Southern Hemisphere than the Northern Hemisphere (Figure 2e), although the standard deviations of the means were not significantly different. The higher mixing ratios in the tropics were from samples collected below 2 km (Figures 3i-3j and Figures 6a-6d). Quantitatively, the mean tropical values for altitudes <2 km were larger with larger standard deviations than those for altitudes >2 km (Table 4). The distribution suggests possible oceanic sources in this region of the tropics for these compounds. We do not believe that biomass burning is a contributor, as we have not seen elevated levels of these gases in our previous studies of biomass burning emissions. The surface mixing ratios and tropical distributions for  $\text{CHBr}_3$  and  $\text{CHBr}_2\text{Cl}$  were similar to those seen by Atlas *et al.* [1993] during a Pacific cruise.

The STRAT upper troposphere measurements of these species were lowest in the tropics relative to the midlatitudes (Table 3). In addition, the tropical STRAT values were substantially less than the >2 km averages from PEM Tropics. Both these observations were presumably due to the higher tropopause altitudes in the tropics, resulting in a greater degree of loss of these species. In the 21–24°N and 36–41°N regions, with the exception of  $\text{CH}_2\text{Br}_2$ , the STRAT mixing ratios were 40–70% smaller than the PEM Tropics values (Table 3). These measurements indicate significant vertical gradients in both the tropics and midlatitudes. The STRAT  $\text{CH}_2\text{Br}_2$  values were comparable to those measured during PEM Tropics (Table 4 and Figure 3i). The  $\text{CH}_2\text{Br}_2$  values were also comparable to measurements near the tropopause from balloon samples in the tropics and high latitudes [Kourtidis *et al.*, 1996].

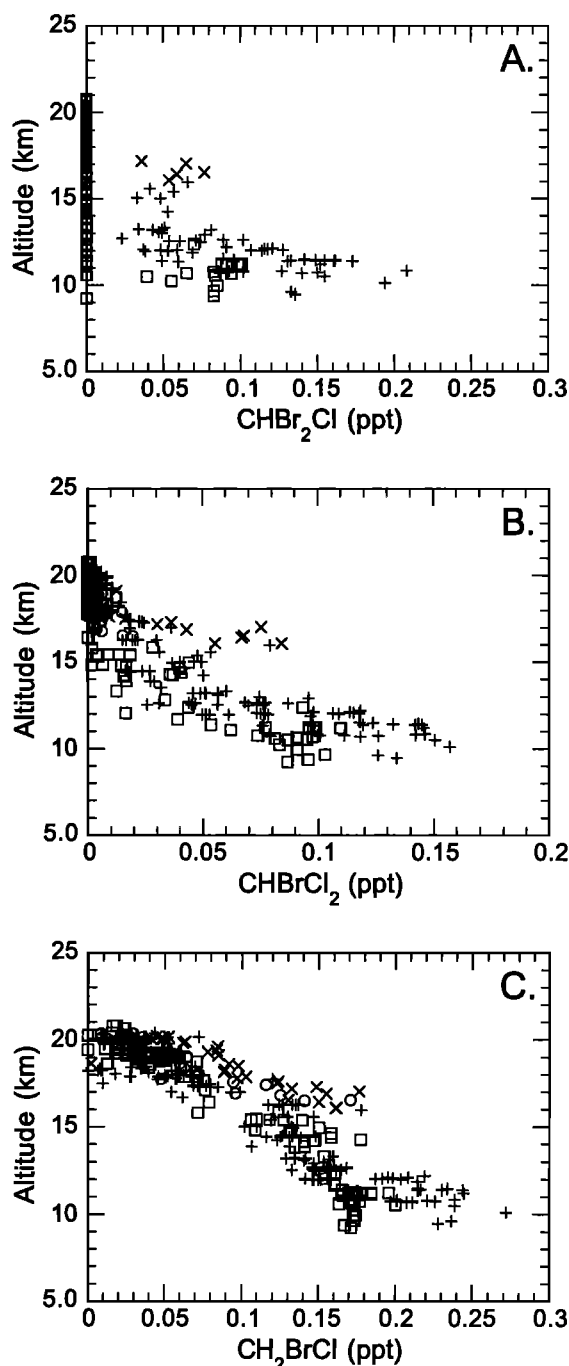
$\text{CHBr}_3$  was the only short-lived compound from the STRAT measurements that showed a difference between the latitude groups, with larger mixing ratios at 34–41°N relative to those at 21–24°N, while the PEM Tropics measurements showed larger mixing ratios in the tropics. The relatively few measurements in this latitude region reported in the literature preclude direct comparison of latitudinal gradients. However, the STRAT values were generally smaller and the PEM Tropics values were comparable to those measured at or near the surface in the Northern Hemisphere [Penkett *et al.*, 1985; Atlas *et al.*, 1993; Yokouchi *et al.*, 1996, 1997] and in the Northern Hemisphere free troposphere [Atlas and Ridley, 1996].

$\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_2\text{Cl}$ , and  $\text{CHBrCl}_2$  mixing ratios from the STRAT and PEM Tropics samples were generally smaller than those measured at the surface [Penkett *et al.*, 1985; Atlas *et al.*, 1993; Yokouchi *et al.*, 1996, 1997] and were within the range observed in the free troposphere [Atlas and Ridley, 1996].  $\text{CH}_2\text{ClBr}$  mixing ratios for STRAT and PEM Tropics were within the range of previously reported tropospheric values [Yokouchi *et al.*, 1994; Atlas and Ridley, 1996].

The STRAT mixing ratios of  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$  in both the tropics and midlatitudes were substantially larger at the tropopause in January than in July (Figure 7). In addition,



**Figure 7.** Vertical distributions from STRAT January (crosses) and July (open circles) samples of (a)  $\text{CH}_2\text{Br}_2$  in midlatitudes, (b)  $\text{CHBr}_3$  in midlatitudes, and (c)  $\text{CH}_2\text{Br}_2$  in the tropics.



**Figure 8.** Vertical distributions from STRAT January tropics (crosses), July tropics (open circles), January midlatitudes (pluses), and July midlatitudes (open squares) of (a)  $\text{CHBr}_2\text{Cl}$ , (b)  $\text{CHBrCl}_2$ , and (c)  $\text{CH}_2\text{BrCl}$ .

$\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$ , and  $\text{CH}_2\text{BrCl}$  mixing ratios from STRAT were also larger in January at both the tropical and midlatitude tropopause (Figure 8). The larger measured mixing ratios of the short-lived species in January may have resulted from relatively recent convective activity in both regions coupled with possible seasonal differences at the surface.

Above the tropopause, mixing ratios of both  $\text{CHBr}_3$  and  $\text{CHBr}_2\text{Cl}$  decreased to zero by 18 km in the tropics and midlatitudes (Figures 3i, 3k, and 8a). At 20 km,  $\text{CHBrCl}_2$  and  $\text{CH}_2\text{BrCl}$  decreased to  $<0.01$  ppt and  $<0.08$  ppt, respectively

(Figures 8b and 8c).  $\text{CH}_2\text{Br}_2$  decreased by 90% or more (to  $<0.2$  ppt) between the tropopause and 20 km in both the tropics and midlatitudes (Figures 3j and 3l). This loss was comparable to that observed by Kourtidis *et al.* [1996] from balloon samples.

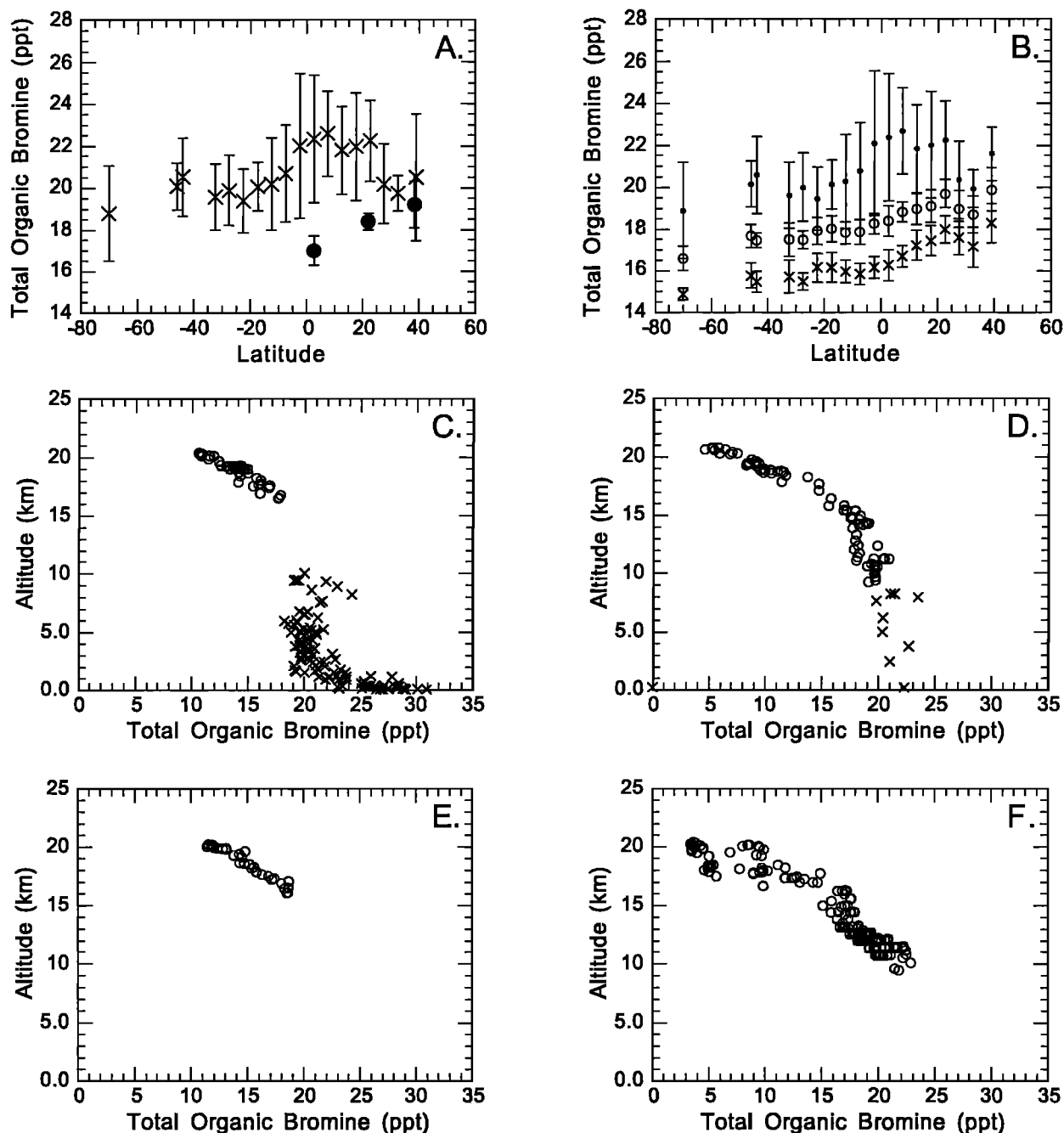
#### 4.4. Total Organic Bromine

The latitudinal distribution of total organic bromine from PEM Tropics samples reflects the combined distributions of the individual species. Larger mean mixing ratios were observed in the  $5^\circ\text{S}$ – $25^\circ\text{N}$  latitude range, although the one standard deviation error bars overlap across the entire latitudinal coverage (Figure 9a). The mean mixing ratio between  $5^\circ\text{S}$  and  $25^\circ\text{N}$  was  $21.9 \pm 0.6$  ppt while the mean of the remaining samples was  $20.0 \pm 0.4$  ppt. The upper troposphere STRAT measurements of total organic bromine from the three latitude regions showed the largest discrepancy with the PEM Tropics samples in the tropical region (Figure 9a). This results from a greater loss of short-lived species in the upper tropical troposphere relative to the midlatitude upper troposphere because of larger levels of OH and the higher tropopause altitude in the tropics which facilitates exposure to elevated levels of radiation. The average mixing ratio of total organic bromine from the PEM Tropics samples was  $20.9 \pm 2.5$  ppt, while the average mixing ratio from the STRAT July/August samples was  $18.5 \pm 0.8$  ppt.

The comprehensive suite of individual species measurements from STRAT provides constraints on the amount of organic bromine in the Northern Hemisphere upper troposphere and at the tropical tropopause. The range of the mean  $\pm 1$  s.d. for total organic bromine from  $21^\circ\text{N}$ – $41^\circ\text{N}$  was 17.0–21.3 ppt and at the tropical tropopause was 16.3–18.7 ppt (Table 3 and Figures 9c–9f; see also Schauffler *et al.* [1998]). The greatest contribution to the variability of the mean values came from the short-lived species. We believe these measurements represent a reasonable range of values for use in stratospheric modeling studies that include bromine chemistry. We caution, however, that for a given convective event which originates over source regions, the amount of organic bromine introduced into the upper troposphere could be substantially greater as a result of the short-lived species (Figures 9b and 11d).

The July mixing ratios of total organic bromine at 20 km in the tropics and midlatitudes were 40% and 75%, respectively, of the tropopause values (Figures 9c and 9d). The January mixing ratios in the tropics and midlatitudes were 38% and 85%, respectively, of the tropopause values (Figures 9e and 9f). As mentioned previously, the higher loss in midlatitudes in January was presumably a result of greater downward transport in the winter midlatitudes.

The percent contribution to total organic bromine by a given species at a given time is dependent on altitude, latitude, and the presence or absence of a tropospheric temporal trend in mixing ratios. Vertical distributions of the fractional contribution to total organic bromine for the major species from the tropical and midlatitude STRAT samples are shown in Figure 10. Methyl bromide represented 55–60% of total organic bromine above the tropopause in both the tropics and midlatitudes (Figure 10d). Below the tropopause,  $\text{CH}_3\text{Br}$  was 50–55% of the total. This reduction was due to the presence of additional species not usually present in stratospheric samples, i.e.,  $\text{CHBr}_3$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$ , and  $\text{CH}_2\text{BrCl}$ . The fractional contribution to total organic bromine for  $\text{CBrF}_3$  increased with altitude (Figure 10a), while that of  $\text{CBrClF}_2$  and  $\text{CBrF}_2\text{CBrF}_2$  decreased with altitude (Figures 10b and 10c). This is a result of the longer lifetime in this region of the stratosphere of  $\text{CBrF}_3$  relative to  $\text{CBrClF}_2$  and



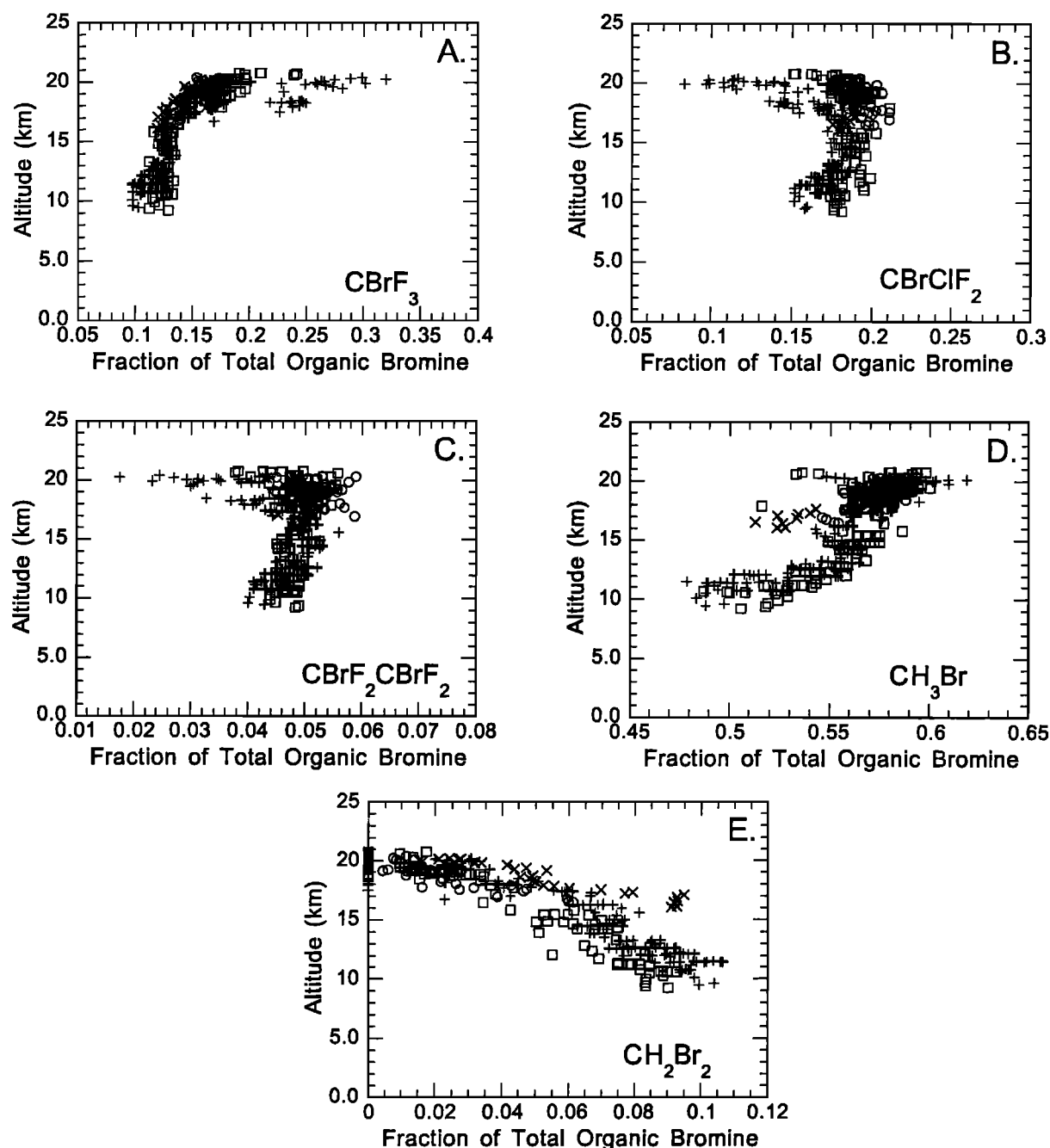
**Figure 9.** Latitudinal distributions of (a) total organic bromine from PEM Tropics samples averaged over 5° latitude bins (crosses) and upper troposphere averaged STRAT samples (solid circles), and (b) averaged PEM Tropics samples subdivided into three groups; the halons and  $\text{CH}_3\text{Br}$  (crosses); the halons,  $\text{CH}_3\text{Br}$  and  $\text{CH}_2\text{Br}_2$  (open circles); and the halons,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_2\text{Br}_2$ , and the short-lived brominated organic compounds (solid circles). Vertical distributions from STRAT (open circles), and PEM Tropics (crosses) of total organic bromine in (c) July tropics, (d) July midlatitudes, (e) January tropics, and (f) January midlatitudes.

$\text{CBrF}_2\text{CBrF}_2$ . The differences in the fractional contributions for the halons between January and July at 20 km were due to sampling of older (more photochemically aged) air in January. The lowest CFC 12 values observed in July were ~380 ppt, while the lowest observed in January were ~230 ppt.

In the tropical lower stratosphere the fractional contribution of  $\text{CBrF}_3$  was 12–18%, while that of  $\text{CBrClF}_2$  was 18–21% and that of  $\text{CBrF}_2\text{CBrF}_2$  was 4.5–5.5%. In the midlatitude lower

stratosphere the fractional contribution to total organic bromine was 12–30% for  $\text{CBrF}_3$ , 10–19% for  $\text{CBrClF}_2$ , and 2–5% for  $\text{CBrF}_2\text{CBrF}_2$ . These values reflect the greater degree of photochemical aging in midlatitude air parcels relative to the tropics. In both the tropics and midlatitudes the fractional contribution to total organic bromine from  $\text{CH}_2\text{Br}_2$  decreased steadily between the tropopause and 20 km from ~9% to ~1% (Figure 10e).



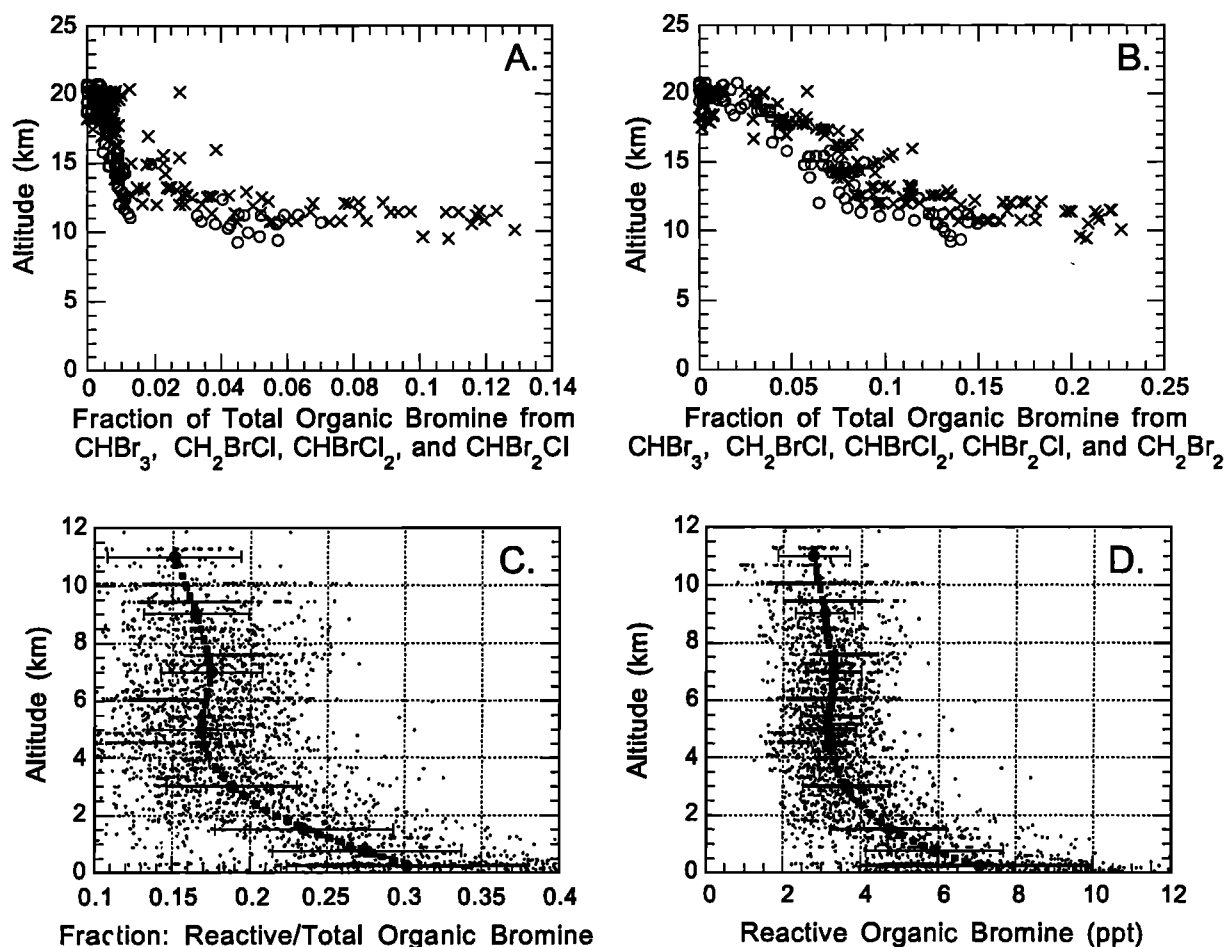


**Figure 10.** Fractional contribution to total organic bromine from STRAT samples from January tropics (crosses), July tropics (open circles), January mid-latitudes (pluses), and July midlatitudes (open squares) for (a)  $\text{CBrF}_3$ , (b)  $\text{CBrClF}_2$ , (c)  $\text{CBrF}_2\text{CBrF}_2$ , (d)  $\text{CH}_3\text{Br}$ , and (e)  $\text{CH}_2\text{Br}_2$ .

The combined fractional contributions to total organic bromine in midlatitudes by  $\text{CHBr}_3$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$ , and  $\text{CH}_2\text{BrCl}$  from the STRAT samples decreased from ~12% at the tropopause to 1% at 20 km (Figure 11a). When  $\text{CH}_2\text{Br}_2$  is included, the STRAT short-lived species contribution to total organic bromine in the troposphere was consistent with the PEM Tropics measurements of ~15% (Figures 11b and 11c). It is important to note that the mixing ratio range of short-lived species at altitudes above 2 km from all PEM Tropics flights was of the order of 2–4 ppt (Figure 11d). The corresponding fractional contributions to total organic bromine were between

10% and 25%. This is consistent with the variability observed in the STRAT tropospheric measurements discussed above. The measurements from both STRAT and PEM Tropics demonstrate the need to use at least  $\pm 1$  ppt uncertainty for total organic bromine when modeling the effects of bromine on stratospheric ozone depletion.

Tropospheric temporal trends in mixing ratios influence the percent contribution to total organic bromine by a given species over time. For example, in winter of 1991–1992  $\text{CH}_3\text{Br}$  was 60.6% of the total organic bromine at the 23°N tropopause, while in 1996  $\text{CH}_3\text{Br}$  was 52.3% of the total at 21–24°N (Table 5).



**Figure 11.** Fractional contribution to total organic bromine from STRAT January (crosses) and STRAT July (open circles) samples from (a) midlatitude short-lived brominated organic compounds, and (b) midlatitude short-lived brominated organic compounds including  $\text{CH}_2\text{Br}_2$ . (c) Fractional contribution to total organic bromine from PEM Tropics samples. (d) Vertical distribution of the short-lived (reactive) compounds from PEM Tropics samples. Dots in Figures 11c and 11d are individual data points, solid circles are averages, and error bars are 1 s.d.

This was due to increased contributions from the halons resulting from increased mixing ratios over time. The longer-lived species tend to contribute a greater percentage to the total organic bromine near the tropopause relative to the mid-lower troposphere because of loss of the short-lived compounds.

#### 4.5. Fractional Dissociation Relative to $\text{CCl}_3\text{F}$ and ODPs

Calculations of ODP [Solomon *et al.*, 1992] and equivalent effective stratospheric chlorine (EESC) [Daniel *et al.*, 1995] require calculation of the fractional halogen release of a given halocarbon relative to the fractional chlorine release of  $\text{CCl}_3\text{F}$ . The fractional chlorine release, FC [Daniel *et al.*, 1995], is defined as

$$\text{FC} = \frac{\mu_{\text{entry},x} - \mu_{\theta,z,x}}{\mu_{\text{entry},x}}$$

where  $\mu_{\text{entry},x}$  is the mixing ratio of halocarbon  $x$  when it enters the stratosphere, and  $\mu_{\theta,z,x}$  is the mixing ratio of halocarbon  $x$  at latitude  $\theta$  and altitude  $z$ . FC represents the fractional dissociation, or amount of halocarbon  $x$  destroyed, between the time of entry into the stratosphere and the time of measurement.

In order to calculate FC for compounds with a temporal trend in the troposphere, the mixing ratios of halocarbon  $x$  and  $\text{CCl}_3\text{F}$  entering the stratosphere must be determined. For the halocarbons of interest here,  $\text{CBrClF}_2$  and  $\text{CBrF}_3$  are the only compounds with a significant increase in tropospheric mixing ratios over the last few years [Butler *et al.*, 1998]. Calculations of the age of air, i.e., the time between entry into the stratosphere and the time of measurement, were based on the relationship between  $\text{N}_2\text{O}$  and age, with age determined from measurements of  $\text{CO}_2$  during STRAT (K. Boering personal communication, 1998). The use of  $\text{CO}_2$  to determine the age of air in the stratosphere is described by Boering *et al.* [1996]. Age of air calculations were used in conjunction with temporal trends of  $\text{CBrClF}_2$  and  $\text{CBrF}_3$  to determine the mixing ratio of these compounds when they entered the stratosphere.

The ratio  $\text{FC}_x/\text{FC}_{\text{CFC-11}}$  is the fractional halogen release of halocarbon  $x$  relative to the fractional chlorine release of  $\text{CCl}_3\text{F}$  and was determined from correlations of FC of the halons and  $\text{CH}_3\text{Br}$  with FC of  $\text{CCl}_3\text{F}$  (Figures 12a-12d). None of the correlations are linear, which means that the fractional dissociation of these compounds is not uniform relative to the fractional dissociation of  $\text{CCl}_3\text{F}$ . Table 6 presents calculations of

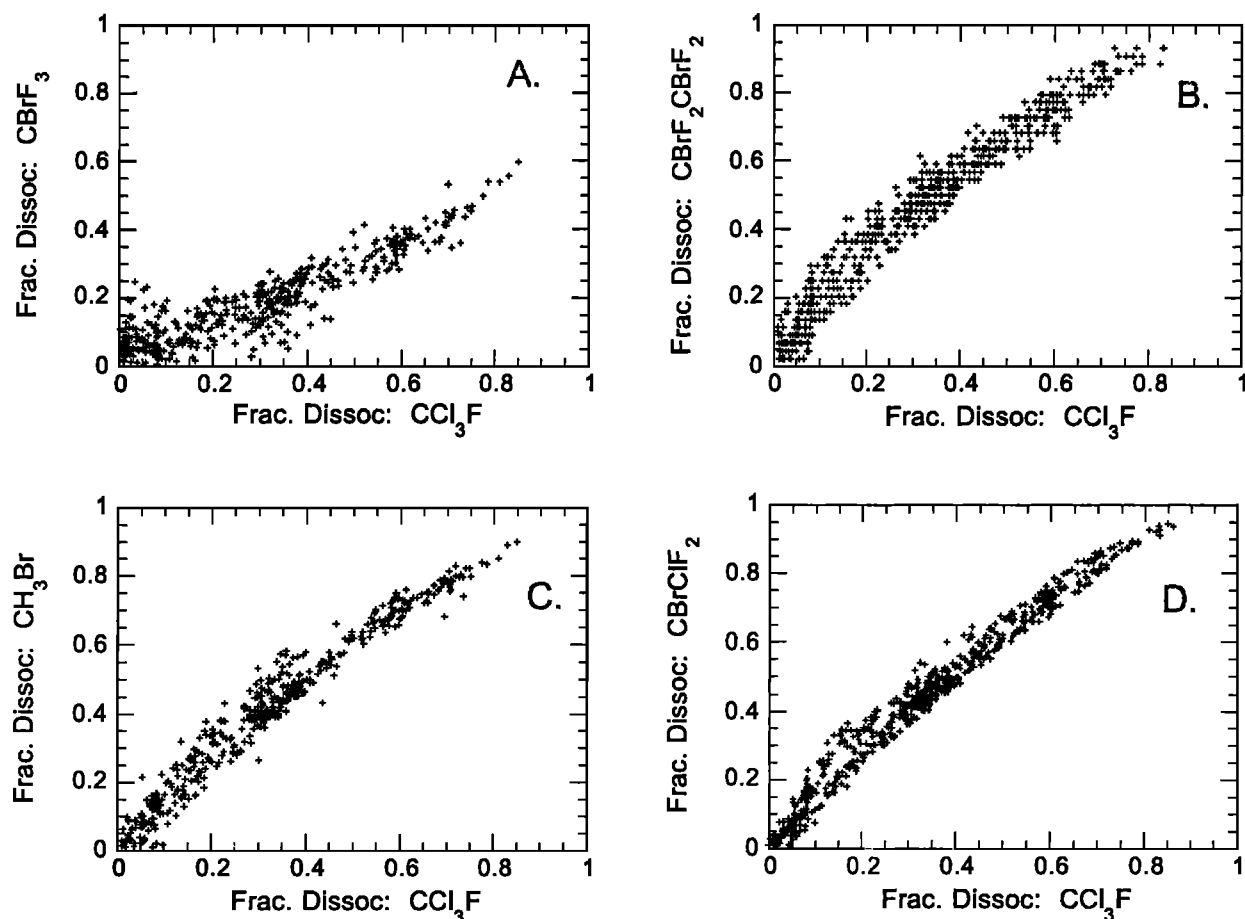
**Table 5.** Percent Contribution to Total Organic Bromine by Each Compound From Airborne Arctic Stratospheric Expedition II, STRAT 21°–24°N, STRAT Tropical Tropopause, and STRAT Troposphere

	CH <sub>3</sub> Br	CBrF <sub>3</sub>	CBrClF <sub>2</sub>	C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub>	CH <sub>2</sub> Br <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	CH <sub>2</sub> BrCl	CHBrCl <sub>2</sub>
AASE II: 23°N tropopause	60.6	11.3	16.3	2.6	9.0				
STRAT 21–24°N troposphere	52.3	12.0	18.4	4.8	8.1	0.9	1.9	0.9	0.4
STRAT tropical tropopause	55.0	13.6	19.8	5.1	5.7			0.7	0.1
STRAT troposphere	52.1	12.0	18.1	4.7	8.0	0.9	3.0	0.8	0.4

AASE II (1992; using recalibrated *Schauffler et al.* [1993] values), STRAT tropical tropopause values are from *Schauffler et al.* [1998].

$FC_x/FC_{CFC-11}$  for the halons and CH<sub>3</sub>Br based on the correlation curves from Figure 12 and on the measurements subdivided by latitude groups of 2°S–10°N, 20–40°N, and 40–60°N.  $FC_x/FC_{CFC-11}$  ratios based on the correlation curves were calculated from a linear correlation within the stated ranges of  $FC_{CFC-11}$ . The appropriate curve was then applied to each sample to calculate the ratio. The  $FC_x/FC_{CFC-11}$  ratios calculated from the measurements were averages of the  $FC_x/FC_{CFC-11}$  ratio from all samples in the stated latitude range. The standard deviations were significantly smaller when the calibration curve was used to calculate the ratio relative to the measured ratios. From the correlation curves the ratio  $FC_x/FC_{CFC-11}$  decreases with increasing  $FC_{CFC-11}$ , i.e., the fractional chlorine release of the halons and CH<sub>3</sub>Br is highest at the lowest fractional chlorine release of CCl<sub>3</sub>F. In addition, we observed a latitudinal dependence of  $FC_x/FC_{CFC-11}$ , with tropical values of the ratio larger than midlatitude values (Table 6). These observations are

a result of variability in the distribution of loss rates with altitude and latitude. In the lower tropical stratosphere the loss rate of CH<sub>3</sub>Br is larger relative to the loss rate of CCl<sub>3</sub>F as compared with the lower stratosphere at higher latitudes so the tropical  $FC_x/FC_{CFC-11}$  is larger. We did not observe significant seasonal differences in  $FC_x/FC_{CFC-11}$  for the halons or CH<sub>3</sub>Br. For comparison we include in Table 6 values from *Pollock et al.* [1992] which were based on measurements from Airborne Arctic Stratospheric Experiment I between 69°N and 79°N and were calculated from  $FC_{CFC-11}$  0.5–1.0. The *Pollock et al.* [1992] CH<sub>3</sub>Br  $FC_x/FC_{CFC-11}$  values are comparable to the values calculated between  $FC_{CFC-11}$  0.53–0.85 from this study. However, the *Pollock et al.* [1992] CBrF<sub>3</sub>  $FC_x/FC_{CFC-11}$  values are larger than the values calculated here, while the  $FC_x/FC_{CFC-11}$  values for CBrClF<sub>2</sub> and CBrF<sub>2</sub>CBrF<sub>2</sub> are smaller. The differences are likely due to uncertainties in the halon entry mixing ratios for 1985 required for the *Pollock et al.* [1992]

**Figure 12.** Correlation between the fractional dissociation of CCl<sub>3</sub>F and the fractional dissociation of (a) CBrF<sub>3</sub>, (b) CBrF<sub>2</sub>CBrF<sub>2</sub>, (c) CH<sub>3</sub>Br, and (d) CBrClF<sub>2</sub>.

**Table 6.** Calculations of the Fractional Dissociation of the Halons and CH<sub>3</sub>Br Relative to CFC-11 (FC<sub>x</sub>/FC<sub>CFC-11</sub>) Using Correlation Curves of FC<sub>x</sub> versus FC<sub>CFC-11</sub> and by Averaging FC<sub>x</sub>/FC<sub>CFC-11</sub> Over Latitude Groups

	CH <sub>3</sub> Br		CBrF <sub>3</sub>		C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub>		CBrClF <sub>2</sub>	
	Average	s.d.	Average	s.d.	Average	s.d.	Average	s.d.
From correlation curves								
Average from all data	1.25	0.14	0.62	0.07	1.41	0.21	1.30	0.13
0.1-0.85 FC <sub>CFC-11</sub>								
Average 0-0.2 FC <sub>CFC-11</sub>	1.57	0.20	0.97	0.36	2.31	1.04	1.60	0.14
Average 0.2-0.4 FC <sub>CFC-11</sub>	1.35	0.04	0.59	0.02	1.54	0.07	1.38	0.04
Average 0.4-0.6 FC <sub>CFC-11</sub>	1.23	0.04	0.57	0.01	1.35	0.05	1.27	0.03
Average 0.6-0.85 FC <sub>CFC-11</sub>	1.10	0.04	0.63	0.02	1.19	0.05	1.16	0.04
Average .53-.85 FC <sub>CFC-11</sub>	1.12	0.05	0.62	0.03	1.22	0.06	1.18	0.05
From measurements								
Average all data, n=958	1.39	0.28	0.68	0.32	1.58	0.44	1.40	0.33
2°S-10°N, n=163	1.71	0.27	0.80	0.42	2.27	0.49	1.71	0.48
20°-40°N, n=580	1.32	0.22	0.68	0.30	1.44	0.19	1.30	0.23
40°-60°N, n=179	1.18	0.07	0.58	0.20	1.34	0.15	1.26	0.15
37°-60°N, n=33	1.19	0.13	0.59	0.20	1.36	0.17	1.28	0.19
Pollock et al. [1992]	1.08	0.14	0.84	0.25	0.92	0.17	1.04	0.12

calculations. The first reported measurements of a temporal trend for CBrF<sub>3</sub> and CBrClF<sub>2</sub> were by Butler et al. [1992] and for CBrF<sub>2</sub>CBrF<sub>2</sub> were by Butler et al. [1998].

The differences in FC<sub>x</sub>/FC<sub>CFC-11</sub> will affect calculations of ODP (and EESC). Table 7 presents ODP calculations using the FC<sub>x</sub>/FC<sub>CFC-11</sub> for the halons and CH<sub>3</sub>Br from the three latitude groups, from 37°-60°N (chosen to represent midlatitudes), and from FC<sub>CFC-11</sub> 0.53-0.85 (the latter value was chosen to correspond to the range used by Pollock et al. [1992]). ODP at a given latitude  $\theta$  and altitude  $z$  was calculated by

$$\text{ODP}(\theta, z) = (\text{FC}_x/\text{FC}_{\text{CFC-11}})(\alpha) [(\tau_x/\tau_{\text{CFC-11}}) \\ (M_{\text{CFC-11}}/M_x)(n_x/3)]$$

or

$$\text{ODP}(\theta, z) = (\text{BEF})(\text{BLP})$$

where  $\alpha$  is the enhanced ability of a bromine atom to destroy ozone relative to a chlorine atom and BLP is the bromine loading potential

$$\text{BLP} = (\tau_x/\tau_{\text{CFC-11}})(M_{\text{CFC-11}}/M_x)(n_x/3)$$

where  $\tau_x$  is the lifetime of species  $x$ ,  $\tau_{\text{CFC-11}}$  is the lifetime of CCl<sub>3</sub>F,  $M_{\text{CFC-11}}$  and  $M_x$  are the molecular weights of CCl<sub>3</sub>F and species  $x$ , respectively, and  $n_x$  is the number of bromine atoms per molecule for species  $x$  [Pollock et al., 1992]. The bromine efficiency factor (BEF) is the product of FC<sub>x</sub>/FC<sub>CFC-11</sub> and  $\alpha$  and represents the amount of stratospheric ozone removed per unit mass of species  $x$  delivered to the stratosphere relative to CCl<sub>3</sub>F [Butler and Rodriguez, 1996]. The ODPs were calculated using a lifetime of 50 years for CCl<sub>3</sub>F [Solomon et al., 1995] and  $\alpha$  of 50 (J. Daniel, personal communication, 1997).

The ODP for each species decreased with increasing latitude as a result of variations in FC<sub>x</sub>/FC<sub>CFC-11</sub> with latitude. The ODPs calculated using the averages from 37°-60°N and from FC<sub>CFC-11</sub>

0.53-0.85 showed a difference of 5-10%, depending on the differences in FC<sub>x</sub>/FC<sub>CFC-11</sub>. The CH<sub>3</sub>Br ODP calculations for 37°-60°N and FC<sub>CFC-11</sub> 0.53-0.85 were 0.40 and 0.38, respectively, which agreed well with the most recent ODP calculation of 0.43 from Butler and Rodriguez [1996] (Table 7). The discrepancy between the current calculations of CH<sub>3</sub>Br ODP and the CH<sub>3</sub>Br ODP calculations from Pollock et al. [1992] and Solomon et al. [1995] was primarily due to the use of a longer lifetime for CH<sub>3</sub>Br in the latter reports. The CBrF<sub>3</sub> ODP calculation from FC<sub>CFC-11</sub> 0.53-0.85 was 12.4, which was comparable to the 12.5 and 12.8 calculations from Pollock et al. [1992] and Solomon et al. [1995], respectively. The ODP values agreed, even though the fractional dissociation reported here was smaller, because of the different values used for  $\alpha$  (Table 7). The ODP calculations for CBrF<sub>2</sub>CBrF<sub>2</sub> for 37°-60°N and FC<sub>CFC-11</sub> 0.53-0.85 were 9.6 and 8.6, respectively, which were larger than the 6.1 calculated by Pollock et al. [1992]. This was a result of the larger FC<sub>x</sub>/FC<sub>CFC-11</sub> and  $\alpha$ , i.e., BEF, used in this report. The ODP calculations for CBrClF<sub>2</sub> for 37°-60°N and FC<sub>CFC-11</sub> 0.53-0.85 were 7.1 and 6.5, respectively, which is also larger than the 4.1 calculated by Pollock et al. [1992]. As with CBrF<sub>2</sub>CBrF<sub>2</sub>, this is primarily a result of the larger FC<sub>x</sub>/FC<sub>CFC-11</sub> and  $\alpha$  used in this report. It is clear from Table 7 that the calculated ODP of a given trace gas is dependent on the values chosen for FC<sub>x</sub>/FC<sub>CFC-11</sub>,  $\alpha$ , and the CCl<sub>3</sub>F and trace gas lifetimes. The fractional dissociation of one trace gas relative to another will vary as a function of the loss distribution of the two gases. A cosine-weighted average of FC will give a global area-weighted average [Daniel et al., 1996]; however, by definition this approach tends to weigh more heavily toward the low latitudes. The greatest loss of ozone is in the mid-high latitudes rather than the tropics, so for global ODP considerations, it seems appropriate to use the FC<sub>x</sub>/FC<sub>CFC-11</sub> values averaged over the mid-high latitudes, which corresponds to the region of greatest loss of CCl<sub>3</sub>F at ER-2 altitudes. The 0.53-0.85 range from the correlation curves represents the average FC<sub>x</sub>/FC<sub>CFC-11</sub> when

**Table 7.** ODP Calculations for the Halons and CH<sub>3</sub>Br Using FC<sub>x</sub>/FC<sub>CFC-11</sub> by Latitude Averages and by Ranges of FC<sub>CFC-11</sub> From the Correlation Curves

	Lifetime of Compound	Lifetime of CFC-11	BLP	Fractional Dissociation	$\alpha$	BEF	ODP	Reference
CH <sub>3</sub> Br	1.3	50	0.013			48.0	0.62	WMO [1995]
	1.5	55	0.013	1.08	40	43.0	0.56	Pollock et al. [1992]
	0.8	50	0.008			54.0	0.43	Butler and Rodriguez [1996]
37-60°N	0.7	50	0.0068	1.19	50	59.5	0.40	this work
0.53-0.85 FC <sub>CFC-11</sub>	0.7	50	0.0068	1.12	50	56.0	0.38	this work
2°S-10°N	0.7	50	0.0068	1.71	50	85.5	0.58	this work
20-40°N	0.7	50	0.0068	1.32	50	66.0	0.45	this work
40-60°N	0.7	50	0.0068	1.18	50	59.0	0.40	this work
CBrF <sub>3</sub>	67	55	0.37	0.84	40	33.6	12.5	Pollock et al. [1992]
	65	50	0.40	0.80	40	32.0	12.8	WMO [1995]
	65	50	0.40	0.59	50	29.5	11.8	this work
37-60°N	65	50	0.40	0.62	50	31.0	12.4	this work
0.53-0.85 FC <sub>CFC-11</sub>	65	50	0.40	0.80	50	40.0	16.0	this work
2°S-10°N	65	50	0.40	0.68	50	34.0	13.6	this work
20-40°N	65	50	0.40	0.58	50	29.0	11.6	this work
40-60°N	65	50	0.40	0.58	50	29.0	11.6	this work
C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub>	26	55	0.166	0.92	40	36.8	6.1	Pollock et al. [1992]
	20	50	0.141	1.36	50	68.0	9.6	this work
	20	50	0.141	1.22	50	61.0	8.6	this work
37-60°N	20	50	0.141	2.27	50	113.5	16.0	this work
0.53-0.85 FC <sub>CFC-11</sub>	20	50	0.141	1.44	50	72.0	10.2	this work
2°S-10°N	20	50	0.141	1.34	50	67.0	9.4	this work
20-40°N	20	50	0.141	1.34	50	67.0	9.4	this work
40-60°N	20	50	0.141	1.34	50	67.0	9.4	this work
CBrClF <sub>2</sub>	19.4	55	0.0980	1.04	40	41.6	4.1	Pollock et al. [1992]
	20	50	0.1108	1.28	50	64.0	7.1	this work
	20	50	0.1108	1.18	50	59.0	6.5	this work
37-60°N	20	50	0.1108	1.71	50	85.5	9.5	this work
0.53-0.85 FC <sub>CFC-11</sub>	20	50	0.1108	1.30	50	65.0	7.2	this work
2°S-10°N	20	50	0.1108	1.26	50	63.0	7.0	this work
20-40°N	20	50	0.1108	1.26	50	63.0	7.0	this work
40-60°N	20	50	0.1108	1.26	50	63.0	7.0	this work

For comparison, we include previously published ODPs. BLP, bromine loading potential; BEF, bromine efficiency factor.

>50% of CCl<sub>3</sub>F has been photolyzed. The use of these values would be consistent with previous ODP calculations of CH<sub>3</sub>Br, CBrF<sub>3</sub> and CBrClF<sub>2</sub> which were based on FC<sub>x</sub>/FC<sub>CFC-11</sub> values obtained from high-latitude samples that corresponded to FC<sub>CFC-11</sub> values >0.5 [Pollock et al., 1992; Butler and Rodriguez, 1996].

## 5. Summary

Measurements of organic bromine compounds from whole air samples collected during the NASA STRAT and PEM Tropics Campaigns in 1996 were utilized to evaluate the following: latitudinal distributions in the troposphere; vertical distributions in the troposphere and lower stratosphere; total bromine values and distributions; the fractional contributions of the individual compounds to the total organic bromine in the upper troposphere and lower stratosphere; the fractional dissociation of the halons

and CH<sub>3</sub>Br relative to CCl<sub>3</sub>F in the lower stratosphere; and the ODP of the halons and CH<sub>3</sub>Br.

The comprehensive latitudinal coverage of PEM Tropics flights allowed us to present the first detailed description of latitudinal distributions of CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>3</sub>, CHBrCl<sub>2</sub>, CHBr<sub>2</sub>Cl, and the halons from 70°S to 40°N. The short-lived species all showed larger mixing ratios in the tropics relative to the midlatitudes of either hemisphere, suggesting marine sources of these trace gases in this region. CH<sub>2</sub>Br<sub>2</sub> also showed slightly larger mixing ratios in the Southern Hemisphere relative to the Northern Hemisphere. The latitudinal gradients of the halons were comparable to their growth rates. The latitudinal distribution of CH<sub>3</sub>Br mixing ratios was comparable to previously measured distributions at the surface and showed a north to south hemispheric ratio of 1.18. The latitudinal distribution of total organic bromine showed larger mixing ratios in the 5°S-20°N region (21.9 ppt) relative to the mean of the

Northern and Southern Hemisphere midlatitude regions (20.0 ppt). The average total organic bromine value from all regions was  $20.9 \pm 2.5$  ppt.

Significant vertical gradients in the troposphere were observed for  $\text{CHBr}_3$ ,  $\text{CHBrCl}_2$ , and  $\text{CHBr}_2\text{Cl}$ . Mixing ratios of these gases were 40–70% smaller in the upper troposphere relative to the lower troposphere. Tropospheric gradients were not evident in vertical distributions of the halons. The tropospheric gradient of  $\text{CH}_3\text{Br}$  mixing ratios was lowest in the tropics with ~3% smaller values in the upper troposphere relative to the lower troposphere, while the midlatitudes showed ~10% smaller values in the upper troposphere. Based on measurements presented here and those previously published, we suggest a likely range for the vertical gradient in  $\text{CH}_3\text{Br}$  of 0–15%. The greatest difference between the lower and upper tropospheric measurements of total organic bromine was found in the tropics and was a result of the greater degree of loss of short-lived species in the upper tropical troposphere. The range of the mean,  $\pm 1$  s.d. for total organic bromine in the upper troposphere from  $21^\circ$ – $41^\circ\text{N}$  was 17.0–21.3 ppt, while the range in the tropics was 16.3–18.7 ppt.

Mixing ratios of the individual bromine compounds decreased between the tropopause and 20 km by differing amounts depending on the season and the stratospheric lifetime of the individual species. All compounds showed slightly higher loss in midlatitudes in January relative to July because of the greater degree of downward transport in midlatitudes in winter. The combined losses of the individual compounds resulted in a loss of total organic bromine between the tropopause and 20 km of 38% in the January tropics, 40% in the July tropics, 85% in January midlatitudes, and 75% in July midlatitudes.

The combined fractional contribution to total organic bromine in midlatitudes by  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ ,  $\text{CH}_2\text{BrCl}$ ,  $\text{CHBrCl}_2$ , and  $\text{CHBr}_2\text{Cl}$  decreased from ~30% near the surface to ~15% at the tropopause. At 20 km the contribution decreased to <4%. Collectively, these compounds represent a significant contribution to tropospheric organic bromine. In the lower stratosphere,  $\text{CH}_2\text{Br}_2$  is the greatest contributor from the short-lived species and represents from ~9% of total organic bromine at the tropopause to <3% at 20 km. In addition, Ko *et al.* [1997] suggest that inorganic bromine from the tropospheric degradation of these short-lived species may be a significant source of bromine to the stratosphere. Based on the difference between tropical surface and tropopause values of total organic bromine, this source could be up to 5 ppt of bromine.

The fractional contribution to total organic bromine by  $\text{CH}_3\text{Br}$  was 55–60% in the lower stratosphere in all samples. The fractional contribution decreased in the troposphere because of the enhanced contribution by short-lived species. At the tropical tropopause the contributions from the halons increased in 1996 relative to 1992, resulting in a decrease in the contribution from  $\text{CH}_3\text{Br}$ .

The fractional halogen release of a given halocarbon relative to  $\text{CCl}_3\text{F}$  ( $\text{FC}_x/\text{FC}_{\text{CFC-11}}$ ) is an important term in calculations of ODP and equivalent effective stratospheric chlorine. Using correlations of the fractional halogen release of the halons and  $\text{CH}_3\text{Br}$  ( $\text{FC}_x$ ) versus the fractional chlorine release of  $\text{CCl}_3\text{F}$  ( $\text{FC}_{\text{CFC-11}}$ ), we calculated  $\text{FC}_x/\text{FC}_{\text{CFC-11}}$ . We found that the  $\text{FC}_x/\text{FC}_{\text{CFC-11}}$  values showed a latitudinal gradient with highest values in the tropics and lowest values in the  $40^\circ$ – $60^\circ\text{N}$  latitude range for all species. We also found that  $\text{FC}_x/\text{FC}_{\text{CFC-11}}$  decreased with increasing  $\text{FC}_{\text{CFC-11}}$ , i.e., we observed the greatest fractional

chlorine release of the halons and  $\text{CH}_3\text{Br}$  at the lowest fractional chlorine release of  $\text{CCl}_3\text{F}$ .

We used the  $\text{FC}_x/\text{FC}_{\text{CFC-11}}$  values to calculate the ODP for each halon and  $\text{CH}_3\text{Br}$  using a  $\text{CCl}_3\text{F}$  lifetime of 50 years and an  $\alpha$  of 50. The ODPs varied in the same manner as the  $\text{FC}_x/\text{FC}_{\text{CFC-11}}$  values. ODPs calculated when >50% of  $\text{CCl}_3\text{F}$  had been photolyzed were comparable to previously published values for  $\text{CH}_3\text{Br}$  and  $\text{CBrF}_3$ , while the ODPs for  $\text{CBrF}_2\text{CBrF}_2$  and  $\text{CBrClF}_2$  were larger. Differences were primarily due to the recalculations of  $\text{FC}_x/\text{FC}_{\text{CFC-11}}$  and the chosen values of  $\alpha$  and lifetimes.

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